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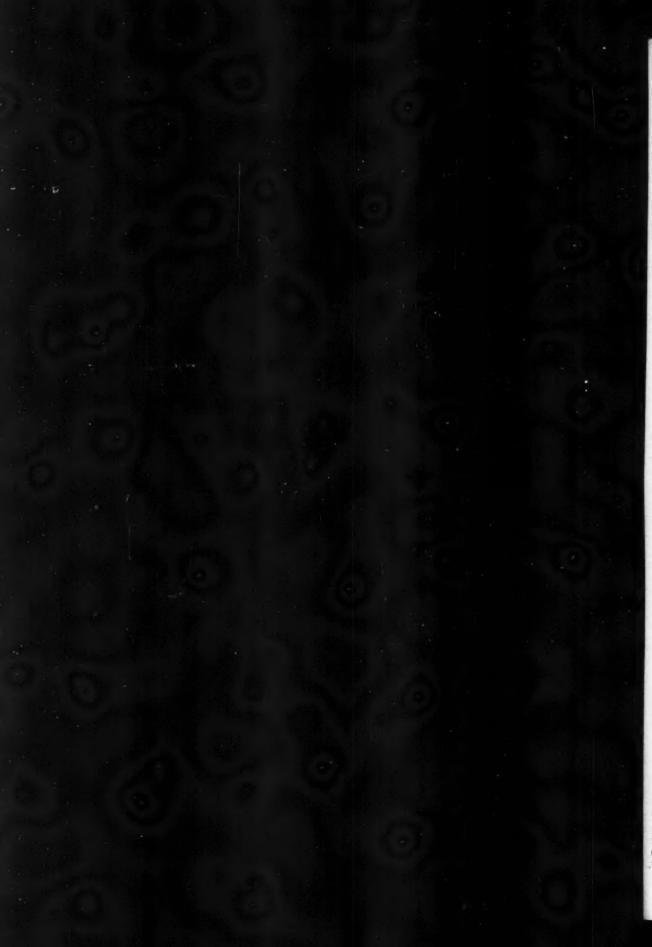
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MANCHESTER SECTION

Meeting in the Gas Department Showrooms, Manchester, on 8th April 1949, Mr. R. J. HANNAY in the chair

The Dyeing of Terylene Polyester Fibre

E. WATERS

The properties of a textile fibre are highly specific, and so we cannot liken Terylene to any other fibre, but for purposes of general comparison it may be said that, being a high-tenacity hydrophobic type of fibre, it most closely resembles nylon. Like nylon it has high tensile strength, is very resistant to chemical and bacterial attack, is circular and uniform in cross section, has low water absorption, and is capable of being set.. The two fibres are not identical in these properties, however, and in many other respects are widely different. For example, Terylene is stronger and has a lower moisture absorption. The main physical features in which Terylene differs greatly from nylon are density, elasticity, handle, and resistance to degradation by light. Terylene is much denser (sp. gr. 1.38 compared with 1.14), it does not stretch as readily, is more pleasant and less cold to the touch, and is much less affected by prolonged exposure to light. Terylene also has a higher refractive index.

Chemically Terylene, being an ester, is most closely related to cellulose acetate, but apart from a certain parallelism in dyeing behaviour the similarity ends here, for Terylene is a very much superior fibre physically. It does not "blind" under the action of heat or water, nor does it saponify readily even with strong alkalis. Terylene is soluble only in the more active types of solvents such as o-chlorophenol, and even in these is less

readily dissolved than nylon.

From a practical point of view, perhaps the most important difference between the accepted textile fibres and Terylene lies in its resistance to dyeing. Terylene cannot be dyed with the same facility as the cellulosic fibres, wool, and nylon, and this paper is an account of work carried out to investigate the dyeing behaviour of Terylene and its practical implications.

THE SEARCH FOR A SUITABLE DYE

At the outset of this work it seemed logical and indeed imperative to examine systematically all the existing types of dye by their appropriate methods of application. However, only the acetate rayon dyes showed appreciable substantivity for Terylene. These are—(1) Duranols and Dispersols, (2) Solacets, and (3) Ionamines, of which (1) are the most important. The Solacets possess less substantivity and are not salt-sensitive as they are on acetate rayon, nor yet acid-sensitive as they are on nylon. The Ionamines, which were the predecessors of the dispersed types, offered little advantage over them in respect of dyeability and were generally inferior in fastness properties.

This investigation further confirmed the early observation that Terylene was a difficult fibre to dye, for even with the preferred Duranol and Dispersol dyes it was clear that acetate rayon and nylon were vastly superior in respect of the ease and rapidity with which the dyes were absorbed. Attention was, therefore, directed to investigating why the new fibre is difficult to dye and to providing

means of improving its dyeability.

THE DYEING CHARACTERISTICS OF TERYLENE

Having established that the dispersed dyes possessed substantivity for the fibre, selected members were used for the purpose of finding whether their poor affinity was due to inability of the Terylene to absorb sufficient dye or whether it was due to the difficulty of the dye in entering and diffusing inside the fibre.

This was determined by measuring both the diffusion coefficients and saturation values of a number of dispersed dyes by measuring the rates of dyeing from an "infinite" dyebath, which involves dyeing a small quantity of fibre in a very large volume of dye liquor, so that even when the

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fibre is saturated the concentration of dye in the liquor is practically undiminished. Under these conditions Hill's equation for free diffusion into cylindrical rods³ may be applied. The rate-of-dyeing curves thus provide data for the calculation of the diffusion coefficients, and if the dyebath concentration is high enough the equilibrium values are saturation values. The estimations were carried out in the normal way by dissolving the dyed fibre in o-chlorophenol and measuring the concentration of the dye in the Spekker absorptiometer. This technique was used by Vickerstaff in his work on the rate of dyeing of dispersed dyes on acetate rayon¹.

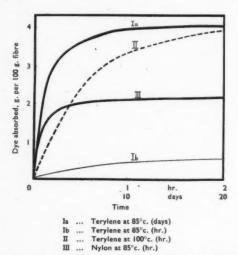


Fig. 1— Rates of Dyeing of Dispersol Fast Orange G 300 Powder Fine

The results were very revealing, for they showed that Terylene is intrinsically a little less dyeable than acetate rayon and superior to nylon. This is illustrated in Fig. 1 and Tables I and II. It will be observed that at 85°c. the relative diffusion coefficients are approximately 1, 500, and 700 respectively, and that raising the temperature from 85°c. to 100°c. produces a considerable increase in diffusion rate, which will be discussed later (p. 612). Undrawn Terylene, which represents the fibre in its least crystalline and least oriented form, is much more readily penetrated, but it is still inferior in this respect to acetate rayon and nylon.

TABLE I

		(1	3/	
Dye	Terylene 85°C.	Nylon 85°C.	Acetate Rayon 85°C.	Terylene 100°c.
Dispersol Fast Orange G 300	4.1	2.1	5-1	4.8
Duranol Red 2B 300	12	4.5	10.8	-
Duranol Violet 2R 300	4-4	4.9	9-4	_
Dispersol Fast Vellow A 300	7:1	5-0	16.0	_

TABLE II

Relative Diffusion Coefficients
(Terylene at 85°c. = 1)

Dye	Terylene 85°C.	Nylon 85°C.	Acetate Rayon 85°C.	Terylene 100°c.
Dispersol Fast Orange G 30	0 1	680	460	48
Duranol Red 2B 300	1	1000	-	_
Duranol Violet 2R 300 .	1	450	****	-

Before considering the more practical and technical consequences, there is one other point of interest in connection with the poor diffusing power of dyes in Terylene, viz. the possible influence of a hard resistant skin on the surface of the fibre. If such a skin were to exist, then a further line of attack on the problem of dyeing would be opened. Evidence undoubtedly exists which indicates that the surface of Terylene fibre does possess physical characteristics different from those of the centre of the fibre; thus it is more birefringent and less readily swollen, but attempts to show that the surface effect has any influence on dyeability or diffusion of dye have been negative. Three main methods were employed in this investigation-(i) to follow the diffusion of the dye through the fibre by microscopic examination of crosssections, (ii) to dye thin cross-sections of the fibre, and (iii) to remove the surface progressively by erosion with alkali and examine the dyeing properties at different stages. In (i) the dyes penetrated smoothly through the fibre, following very accurately Hill's diffusion equation, and final dyed sections showed no difference in intensity across the faces of the sections. Similarly, in (ii) the crosssections were uniformly dyed, and no indication of a readily penetrated core was obtained. The

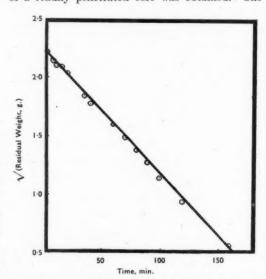


Fig. 2— Rate of Hydrolysis of Terylene (2 denier per filament) with 20% Caustic Potash at 98° C.

third experiment (iii) was carried out as a result of hydrolysis experiments with caustic alkalis, which had shown that hydrolysis of the fibres produced smooth erosion of the filaments, which gradually became finer and finer and yet remained quite smooth, circular in cross-section, and of similar tenacity in grams per denier to the original fibres. This yielded a method of removing any desired depth of surface, and dyeings were carried out on a range of treated fibres. No increase in dyeability other than that expected from the increased surface area was observed, and as the rate of hydrolysis with the alkali was also found to be constant, a

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double confirmation of the negligible effect of any skin on the dyeing or aqueous treatment of Terylene was obtained. We must conclude that the influence of any surface skin, if such exists, is negligible.

TABLE III

Dycing of Terylene after Hydrolysis
(20% caustic potash at 100°C.)

	-		
Time min.	Loss in Weight	Dye U	ptake (%) Calculated
0	_ *	10	10
30	42	12	18
45	85	18	25

Table III and Fig. 2 show the effect of erosion on dyeability and on the rate of hydrolysis respectively. The photomicrographs of fibre cross-sections in Fig. 3 show the smooth progress of dye through the fibre.

The observation that slow diffusion is the cause of the poor dyeability of Terylene in the technical sense enables us to suggest possible ways in which it may be improved. We can—

- (a) Select or devise more readily diffusible dyes
- (b) Open up the fibre or otherwise modify it to increase rate of diffusion
- (c) Vary the dyeing technique to produce the most favourable conditions for diffusion.

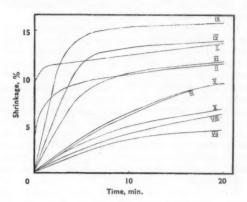
A combination of (a) and (c), whereby selected dyes are dyed under the most favourable conditions and a special azoic technique has been employed for heavy dyeings, has provided the greatest degree of practical success, but it is intended to deal with one aspect of (b) first. This is the process of dyeing in the presence of swelling agents or "carriers", which swell the fibre and thereby aid diffusion and dyeing.

CARRIER DYEING

The addition of an agent to the dyebath to produce a desired effect, whether it is to induce levelling, increase penetration, promote wetting, increase exhaustion, confer good "handle", or kindred other functions, has long been the practice of the dyer, and the principle is well established. It is natural, therefore, that the observation that certain chemicals increased markedly the uptake of dispersed dyes by Terylene was followed by an extensive search for suitable dyeing assistants or carriers.

The types of compound possessing good carrier action, as measured by the increased rate of dyeing, can be divided into four main groups—phenolic substances, primary amines, hydrocarbons, and ethers. In all groups aromatic derivatives are greatly superior to aliphatic ones. Typical members of each class are m-cresol, s-trichloroaniline, chlorobenzene, and β -naphthyl methyl ether. Since all active compounds are capable of swelling the fibre and ultimately causing relaxation, it seems highly probable that they operate by opening up the internal fibre structure and permitting diffusion to occur more readily.

The practical effectiveness of a compound is not, however, solely a function of its swelling efficiency, for a series of compounds whose swelling action was measured quantitatively from solutions in organic solvents did not fall into the same order as that given by dyeing experiments (Fig. 4)². The influence of the dyebath in determining the distribution of agent between water and fibre is certainly an important factor, and this, no doubt, accounts for the fact that compounds possessing ionisable or solubilising groups are notably ineffective. Thus benzoic acid is much inferior to benzene, β -naphtholsulphonic acid to β -naphthol, and β -naphthyl β' -hydroxyethylether to β -naphthyl methyl ether.



Increasing Effectiveness as Carrier-

1	***	Phenol	VI		Quinol Dimethyl Ether
11		p-Octylphenol	VII		cycloHexylphenol
111		m-Cresol	VIII		β-Naphthol
IV		o-Chlorophenol	DX.	000	2:5-Dichloroaniline
V		a-Nitrophenol	×		p-Hydroxydiphenyl

Fig. 4— Action of Swelling Agents on Terylene

The influence of solubility in the dyebath is also illustrated by the fact that if Calsolene Oil HS, which acts as a solubilising agent on m-cresol, is added to the dyebath, the carrier efficiency of the m-cresol is reduced; while if caustic soda is added in sufficient quantity to dissolve the m-cresol, the carrier action is completely inhibited.

It is possible, however, to get a reversal of this effect in a series of increasing molecular weight. Thus we have the following series, in which the middle component is superior to those on either side—

Phenol < o-Chlorophenol > PentachlorophenolPhenol < p-tert.-Butylphenol > p-Octylphenol

 β -Naphthol < Bromo- β -naphthol > Dibromo- β -naphthol

Substances of high molecular weight tend to deposit on the surfaces of the fibres, and it is considered that the initial effect of increasing molecular weight is to reduce the solubility in water and thereby increase efficiency as a carrier. Increasing the molecular weight still further, however, will reduce the rate of diffusion of the carrier into the fibre, and ultimately prevent entry altogether.

The most effective agent on an efficiency/weight basis is β -naphthyl methyl ether, but mere efficiency is not the only criterion of practical suitability, and further examination of the carrier

types showed that the four main groups may be further condensed into two groups—active and inert. The phenols and amines readily form salts with alkalis and acids respectively, and these, being water-soluble, are completely devoid of carrier action. By the addition of alkali or acid, the action can be killed at the end of dyeing, and the carrier then removed from the fibre by scouring. It is obviously desirable to remove excess carrier, but in the case of the ethers and hydrocarbons no means of neutralising the carrier action is available, and in the afterscouring treatment a considerable amount of dye is removed with the carrier.

In any case, the complete removal of any carrier by a simple treatment has proved very difficult, and residual phenolic and amino compounds have a deleterious effect on light fastness, as well as being potentially dermatitic. The results of these investigations show that, of the compounds possessing carrier action, the phenols appear the most practicable, but as further evaluation has failed to find a more economical agent than m-cresol (which requires a dyebath concentration of 2% to be really effective), and as the carriers themselves are very temperature-sensitive and operate only above 70°C., none of them can be recommended for general use.

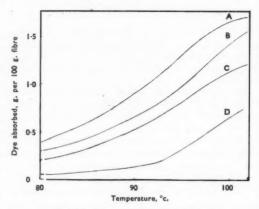
Other undesirable features are volatility in steam, shrinkage and relaxation effects on the yarn, and odour both during dyeing and in the

Although some 300 different compounds have been examined as carriers, none has proved to be at once sufficiently effective and yet free from the hazards just mentioned to make it worthy of general recommendation. This still leaves the probability that carriers will find their application in specific cases, e.g. in printing or for producing heavy dyeings.

DYES FOR TERYLENE

It was stated earlier that for practical working a combination of selected dyes and selected dyeing conditions was essential to obtain the optimum results when dyeing Terylene. We shall therefore consider the practical dyeing behaviour of Terylene with respect to the dispersed acetate rayon dyes. The two most important factors are the temperature of dyeing and the choice of dye. It will be remembered that the rate of diffusion of Dispersol Fast Orange G 300 Powder Fine was very much greater at 100°c. than at 85°c. (Table II), so much greater that it must be supposed that the fibre is opened up at the higher temperature, and this effect of temperature is continued above 100°c. (Fig. 5) It will be seen that above 85°c. the curves rise steeply, every degree rise from 85°c. to 100°c. being important. This gives us the key to what must be done in practice—the dyebath temperature must be as high as possible, preferably at the vigorous boil, and equipment in which the cloth or yarn is immersed for the most part in the dye liquor must be used. Little difficulty is, therefore, to be expected in yarn dyeing, while in piece dyeing a winch will have a considerable advantage over a jig, and a closed machine over an open one.

The behaviour of the individual Dispersol and Duranol dyes on Terylene resembles their behaviour on acetate rayon in that the rapid-dyeing types on acetate rayon are the most suitable for dyeing and building up on Terylene. The slow diffusion through the fibre, however, causes Terylene to bring out more sharply the differences in the dyeing properties of the various dyes, and many of the slower-dyeing members are of little value in practice.



A Duranol Red 2B 300 C Duranol Blue GN
B Dispersol Fast Orange G 300 D Dispersol Fast Scarlet B 300

Fig. 5— Temperature Range of Dispersed Dyes on Terylene

(All dyes Powder Fine, dyed for 90 min. at 30: 1 liquor ratio)

Selected dyes for the dyeing of Terylene are-

Dispersol Fast Orange G 300 Powder Fine Duranol Orange G 300 Powder Fine Dispersol Fast Yellow G 300 Powder Fine Duranol Red 2B 300 Powder Fine Duranol Red GN 300 Powder Fine Duranol Brilliant Violet B 300 Powder Fine Duranol Violet 2B 300 Powder Fine Duranol Bite GN Powder Fine

With these dyes at the boil a very wide range of hues can be obtained up to medium depths. For the production of the really heavy dyeings the limitation of the blues becomes very apparent, and it is impossible to get full tertiary shades other than orange-browns by direct dyeing. Even with the browns, which rely on the good dyeing properties of the oranges and reds, the process rapidly becomes uneconomical in the deeper shades on account of the low degree of exhaustion. It is not possible to produce blacks, deep scarlets, or navy blues by direct dyeing.

When dyeing Terylene with dispersed dyes the usual dispersing agents such as Dispersol VL are found to be advantageous, and in view of the slow rate of dyeing below 85°c. there is no point in starting dyeing below 80°c. There is in fact an advantage in starting at high temperatures, since the dye is then in a better state of dispersion. Two important consequences of the slow rate of dyeing of Terylene are that its level-dyeing properties are very good and that its level-dyeing properties are poor. It is, therefore, relatively easy to obtain uniform

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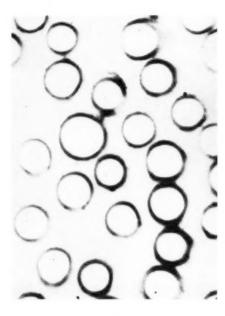
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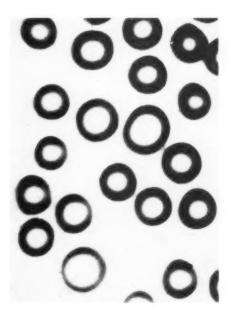
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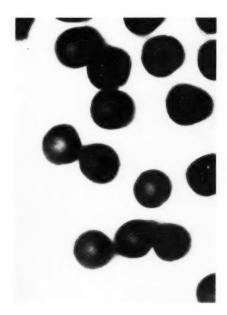
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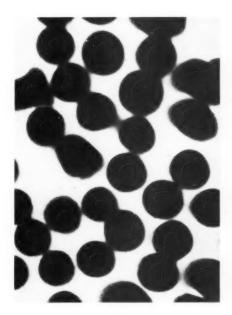
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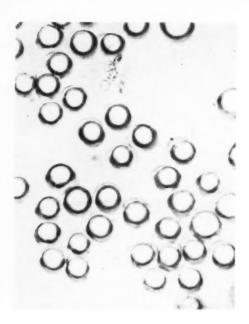


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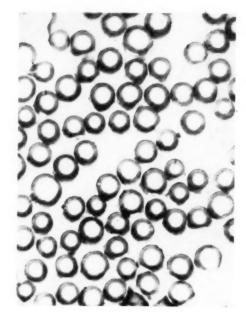


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Fig. 3— Uniform Progress of Dispersol Fast Orange G through Terylene Fibres. Cross-sections \times 370



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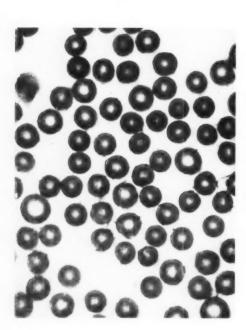
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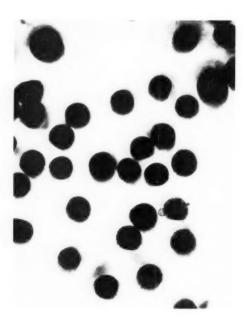
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Fig. 6 — Cross-sections of Azoic-dyed Terylene–Fibres (Brentamine Fast Bordeaux coupled with 2:3-hydroxynaphthoic acid, dyed by modified technique) showing Greater Rate of Diffusion compared with Dispersed Dyes (Fig. 3). \times 370

results by controlled dyeing but difficult to correct faulty dyed material. The package dyeing of cheeses, which always entails some levelling from one region of the package to another, cannot be successfully effected in under three hours at the boil.

The fact that winch dyeing or beck dyeing at the boil is recommended for the dyeing of Terylene raises the very important question of the effect of boiling in rope form on the setting of the material. We know that flat nylon piece goods would not stand up to this treatment, but laboratory tests have shown that Terylene can be finished in a crease-free state after winch dyeing. From these tests and further small-scale experiments on the setting of Terylene, it would appear that this fibre is not set as readily as nylon, and in consequence is less liable to be permanently creased in the dyebath. Some setting treatment is advisable, however, to stabilise stitch formation in knitted goods and to promote dimensional stability in woven goods. Conventional nylon practice may be satisfactory for this purpose, but much bulk-scale experience is required before the question of conditions for adequate setting can be settled.

The properties of the dispersed dyes when on the fibre are much as one would expect from their behaviour on acetate rayon, but there are certain differences. The dyed Terylene is more resistant to washing and to gas fume fading than acetate rayon and resembles nylon in this latter respect. The shade and fastness to volatilisation are very much the same as on acetate rayon. In respect of light fastness the behaviour, as is often the case with the same dyes on different fibres, is anomalous. On the whole the order of fastness is similar on the acetate and Terylene, but individual dyes may be less fast or faster without apparent reason. On Terylene the Duranol reds are superior, and the Dispersol reds inferior, but the blues are the main difficulty. Very few Duranol blues are as fast to light on Terylene as they are on acetate rayon or nylon. This is due not so much to loss of colour as to a marked tendency to redden in hue after quite short exposures. This effect is noticeable with acetate rayon, but is more pronounced with Terylene. The most satisfactory of the blues with good dyeing properties is Duranol Blue GN, which has better light fastness on Terylene than on acetate, and for this reason is the recommended blue component in mixtures. For general mode shades the combination recommended is-

> Dispersol Fast Orange G 300 Powder Fine Duranol Red 2B 300 Powder Fine Duranol Blue GN Powder Fine

and the blue is the slowest-dyeing member. With this recipe medium shades of light fastness 4–5 on the S.D.C. scale can be obtained. The inclusion of Duranol Brilliant Violet B in the place of the blue would produce a more balanced dyeing combination, but the light fastness would be very much reduced.

THE MODIFIED AZOIC PROCESS

The main problem of direct dyeing is the production of the really deep shades, and for this we must turn to a modification of the azoic process,

which has been found readily to yield very deep reds, maroons, blues, and blacks.

Once it had been accepted that any method of increasing diffusion would lead to better colour value on Terylene, it followed that a promising line of attack would be to employ the simpler dye components themselves and form the dye in situ. Having in mind the observations on carrier dyeing that simple phenolic and primary amino compounds possessed good affinity for Terylene and diffused rapidly to the centre of the fibre, it was natural that attempts should be made to apply the azoic process.

When, however, the normal process was carried out, applying the Brenthol as the sodium salt and then aftertreating with the diazotised base or stabilised diazonium salt, no coloration was obtained. Remembering the effect of caustic soda in inhibiting the carrier action of m-cresol, the next step was to try applying the Brenthol as the free acid and then coupling as before. Again no success was achieved, and only faint coloration was obtained when both the Brenthol and the free base were applied as dispersions and attempts made to diazotise and couple in situ. It was finally considered that the lack of success might be due to the high molecular weight of the Brenthols, whose affinity was offset by a very slow rate of diffusion or even inability to enter the fibre. This line of reasoning was substantiated to some extent by the fact that when the Brenthol of lowest molecular weight was used (Brenthol AS) a slight but definite coloration was produced.

Attention was then given to smaller and simpler naphthols such as a-naphthol, β -naphthol, and 2-hydroxy-3-naphthoic acid. Immediately good results were achieved by the technique of applying the amine and naphthol as dispersions and subsequently diazotising. It was necessary, however, to carry out the diazotisation hot in order to get satisfactory results. This was attributed to the low rate of penetration of the nitrous acid into the fibre at low temperatures, but later work has shown that diazotisation will occur cold in a reasonable length of time and that high temperatures are required for complete coupling. The Brentamine Fast Bases, which couple readily on cotton, are, therefore, those which work most satisfactorily in the modified azoic process. For this reason most of the reds couple under quite widely varying conditions of diazotisation, but the blues and violets are much more sensitive to the pH of the coupling bath. With Brentamine Fast Violet B Base greatly enhanced colour value is obtained, for example, if diazotisation is carried out cold and coupling effected in a fresh, hot, slightly alkaline bath.

Of the naphthols tried in this technique the 2-hydroxy-3-naphthoic acid proved to be the most suitable, readily yielding pure bright shades with all the Brentamine Fast Bases. Photomicrographs of cross-sections for a typical combination are illustrated in Fig. 6 and show the much greater rate of penetration compared with the dispersed dye in Fig. 3.

Selected bases for this process are listed in Table IV.

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TABLE IV

rejected Duses for the Martin Di	errift o	resystems
Base		Light Fastness*
Brentamine Fast Red B Base		6
Brentamine Fast Scarlet G Base		4-5
Brentamine Fast Red GL Base		5-6
Brentamine Fast Red 3GL Base	***	5
Brentamine Fast Bordeaux GP Ba	80	3-4
Brentamine Fast Corinth LB Base	***	3
Brentamine Fast Blue B Base	***	2-3
Brentamine Fast Violet B Base		2
Paranitraniline S		6
Dispersol Diazo Black 2BS Powder	Fine	6
· Combination with 2:3-Hydroxy		oic acid

The last product, Dispersol Diazo Black 2BS Powder Fine, is worthy of special notice, since it yields dark navy blue to black shades of exceptionally good fastness when dyed by the modified azoic process. It possesses one technical disadvantage, however, in tending to cause tarring in the dyebath when added to 2-hydroxy-3-naphthoic acid, a problem still under investigation.

The normal yellow-producing azoic components do not respond to this modified azoic technique, and satisfactory yellows cannot yet be produced in

this manner. In view of the undoubted value of this azoic method of application, the fastness properties of the coloured Terylene are naturally of great interest, and an examination of the washing and light fastness properties of the various combinations has been made. All combinations are extremely fast to washing, and the normal finishing treatment recommended is to boil in alkaline soap solution. This treatment emoves only the surface pigmentation, and very little of the fixed colouring matter can be washed out. As far as light fastness is concerned, the combinations vary amongst themselves in fastness, as with cotton. Some are relatively low-only 3-4 on the S.D.C. scale-but the majority are over 4 and selected combinations are as high as 6. The red produced with p-nitroaniline and the blues and blacks obtained with Dispersol Diazo Black 2BS are rated over 6 in light fastness (Table IV).

CONCLUSION

Future developments must certainly lie in the extension of both dispersed acetate rayon dyes and components for the modified azoic process, and possibly in the exploitation of high-temperature dyeing. In particular, increased light fastness and rate of dyeing are desirable.

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References

- ¹ Vickerstaff, T., J.S.D.C., **59**, 92 (1943).
- ² Carlene, P. W., Unpublished work.
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Discussion

Mr. H. A. TURNER: Since Terylene is unique among fibres in that the fibre substance contains an aromatic building unit, how far is it possible to

assist dyeing by the introduction of active chemical groups, e.g. basic or acidic groups, into the terephthalic nucleus through reactions carried out after the fibre has been spun?

Mr. WATERS: The Terylene fibre, having a highly oriented structure, is not readily reactive, and it is difficult to produce chemical variations without damaging the fibre. Sulphonation has been tried with very limited success.

Mr. L. W. Pickup: Does the fastness to light of dispersed acetate dyes on Terylene differ according to whether the fibre is dyed at 85° or 100°c., and does it depend on the diffusion of dye into the fibre?

Mr. Waters: There is some evidence that light fastness tends to be lower on the dyeings which are less penetrated, but this effect is very slight indeed. This is really only noticeable when the dye is purely on the surface, and no practical difference was observed with the preferred dye at 85° and 100°c.

Dr. A. F. Kertess: Can Terylene fabrics be printed?

Mr. Waters: Owing to the lack of Terylene fabric, little work has been done on printing, but the most satisfactory technique so far seems to be to print normally with dispersed dyes and to follow by pressure steaming at 10–30 lb./sq. in. in batch form. The use of some carrier technique might be more promising in the case of printing.

Mr. H. A. Turner: Is it not more easy to get the high temperatures, shown to be so important in the application of acetate dyes, by steaming than by any process normal in dyeing? Further, since dyes in printing are applied at much higher concentrations than in dyeing, leading presumably to their presentation in a less fully dispersed condition, might it not be expected that the properties of the Solacets would show less differentiation from the dispersed type? Do experimental results confirm

Mr. WATERS: Printing does lend itself more readily to high-temperature processing, and the dispersed dyes do print well if thoroughly steamed afterwards under pressure. The Solacets have less affinity and do not print well. Normal open steaming produces indifferent fixation, and static pressure steaming is much superior.

Mr. F. CROMPTON: Has Terylene any reducing action? Would not the *m*-cresol carrier agent prevent diazotisation?

Mr. WATERS: No reducing effect has been observed with Terylene. m-Cresol should not normally prevent diazotisation, but it is not used in the modified azoic technique because of the possibility of cross-coupling.

Dr. W. L. LEAD: Has the lecturer any experience of the dyeing properties of undrawn Terylene? In other words, how does the degree of orientation affect rate of diffusion, etc.?

Mr. Waters: The degree of orientation does affect the rate of diffusion and, as shown in the diagrams, undrawn (i.e. unoriented) fibres do dye much more readily. Undrawn Terylene at 85°c. does not dye quite so rapidly as acetate rayon.

Mr. F. Grainger: Do the dispersed acetate oranges and reds give a different shade on Terylene from that normally obtained on acetate rayon?

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dyes on Terylene, unlike those on nylon, are very similar to the shades on acetate rayon.

W. BRADLEY: Would there not be difficulty in matching a pattern due to the pronounced effect of the temperature gradient between 95° and 100°c., particularly in heavier dyeings?

Mr. WATERS: The matching of a shade should not be unduly difficult, but it could be influenced by temperature variations. The slow rate of dyeing should allow fair latitude in matching up.

Dr. C. M. WHITTAKER: Regarding Mr. Waters'

Mr. Waters: The shades of the dispersed acetate modified azoic process, several years ago it was the practice in Yorkshire of at least one cotton warp dyer when dyeing Primuline Red on highly twisted warps to run the diazotised Primuline into the boiling β -naphthol developing bath, in which it was claimed that better penetration was obtained. This raises the point as to whether the application of an old dyeing technique to a new fibre is patentable: my legal advice is that it is not.

Mr. WATERS: The technique differs radically from other earlier similar processes, and has been accepted by the Patents Office.

COMMUNICATIONS

Absorptiometric Colorimetry*

C. H. GILES

This review is an attempt to bring together, for the benefit of the many users who may not have the time and facilities to consult all the original sources, a short account of the basic principles of the operation and construction of absorptiometric colorimeters, and of their historical development, and to offer a guide to the wider literature on the subject†. Descriptions are given of—the Beer-Lambert laws, photoelectric cells and absorptiometric colorimeters incorporating them, the various types of visual comparison instruments, apparatus for making continuous measurements, the reasons for the use of colour filters and their correct selection, the determination of coloured substances in mixed solution, the accuracy of absorptiometric designations described future developments and their correct selections. absorptiometric colorimeters, desirable future developments, and terminology.

Introduction

A series of solutions of a coloured substance may be compared and their strengths exactly measured relatively to each other by comparing their transmissions of light, or the inverse, i.e. their absorp-The process is termed absorptiometric colorimetry and the instruments used are known either as absorptiometric colorimeters, or as colour comparators, filter photometers, absorptiometers, or simply as colorimeters**. In such measurement it is not usually necessary to determine the light absorption at every part of the spectrum. If such information is required, it may be obtained by using a spectrophotometer, an instrument in which white light is divided into a spectrum by a prism. A spectrophotometer can be used also as an absorptiometric colorimeter, by setting it to measure light absorption at a given wavelength, chosen according to the characteristics of the solutions under test, and examining their absorptions at this wavelength.

Normally, however, specially designed instruments are employed for absorptiometric colori-In these the required comparisons are made either by direct visual observation, or by the action of the transmitted light on a photoelectric cell, which is a device giving an electric response varying with the intensity of the light falling on it. The photoelectric type of absorptiometric colorimeter has now become an important item of equipment in laboratories where chemical analyses are performed. Many analytical methods are simplified by its use, enabling economies in time and materials to be effected. It is widely used in routine medical and biological testing, in many forms of organic, metallurgical, and general inorganic analysis, and in the colour-making and colour-using industries. It is also of importance as an analytical instrument in many forms of scientific research.

Historical Development

FUNDAMENTAL LAWS

The principles of all forms of colorimetry are based on exact knowledge of the general laws of light transmission and absorption, and of the com-position of the spectrum. It was not until about the middle of last century that such knowledge began to be acquired.

Fraunhofer (1821), Bunsen and Kirchhoff (1860), and Angström (1868) were among the pioneers in determining wavelengths of characteristic lines in emission spectra, and in laying the foundations on which the modern science of spectrophotometry has been built. During this early period there was completed the discovery of the simple mathematical principles governing the absorption and transmission of light by transparent substances. Some of these principles had been suggested by the work of Bouguer more than a century earlier.

Bouguer, who may be considered the real founder of this science of exact light measurement, carried out his researches at le Havre and in 1729 published them in a book entitled Essai d'Optique, sur la Gradation de la Lumière 51. He investigated the attenuation suffered by light in passing through

[•] This paper is based on a lecture given to the Scottish Section of the Society of Dyers and Colourists, at the Royal Technical College, Glasgow, on 16th December 1947, Mr. J. A. Young in the chair. This lecture was also read in absentia before the New South Wales Section of the Society of Dyers and Colourists of Australia at Sydney on 17th November 1949, Mr. G. ATHOL BURNS being in the chair.

[†] Practical aspects of the use of these instruments in textile and dye chemistry will be the subject of a later publication.

^{**} For a fuller discussion of the terminology of this subject see p. 628.

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different thicknesses of glass plates, and formulated a law that this weakening depends logarithmically upon the thickness of the glass. Lambert in 1760 redefined this law in more exact mathematical terms; it has consequently come to be generally known as Lambert's law. Beer?, working at Bonn in 1852, discovered the corresponding relation between light absorption and the concentration of a coloured solution. These observations, made though they were with simple apparatus, were precise and fundamental. They laid the foundations of modern quantitative colorimetry.

VISUAL COMPARISON OF COLOUR STRENGTH

Spectrophotometric analysis may be said to date from 1871, for in that year Vierordt⁵⁰ devised a method of comparing the strengths of two coloured solutions by placing them in front of variable-width slits arranged to lie in the plane of the spectrum image in a spectroscope, and in 1873, in Germany, the first textbook on spectrophotometric analysis appeared⁵. The subject steadily developed from that time onwards. The related branch of science dealing with quantitative analysis by colorimetric methods has been somewhat slower in its growth.

In 1854, soon after Beer published his original observations, an instrument was invented in France which utilises the principle of Beer's law75. This is the well known Duboscq colorimeter for visual comparison of the strength of coloured solutions. For a long time thereafter, little further advance seems to have been made. This was probably due both to the lack of reagents suitable for colorimetric analysis and to the absence of stable and convenient sources of artificial illumination. Many varieties of colorimeter of similar design to the Duboscq appeared in later years, however, and in comparatively recent times several advanced designs of visual instrument have been produced. Thus, in 1925 Carl Zeiss A.-G. introduced the Pulfrich photometer, an elaborate instrument of high precision, and in 1933 E. Leitz A.-G. introduced the Absolute Colorimeter. Instruments of these types probably represent the highest degree of precision attainable in visual comparison equipment, the accuracy of which is, of course, limited by that of the human eye.

Colorimetric analysis which does not depend for its accuracy on the eye came within the bounds of possibility only when photoelectric cells of reliable performance were obtainable. Such cells have been available only during the past three or four decades, though the principles on which they operate have been under investigation for a much longer period.

PHOTOELECTRIC PHENOMENA

Becquerel⁶ (1839) noticed that a potential difference is generated between two metal electrodes placed in an electrolyte when light falls on one of them; Willoughby Smith (1872) discovered a change in the electrical resistance of selenium when it is illuminated; and Hertz (1887) noticed that light can release a negative charge held by a metal surface in air. This last effect was investigated in more detail by Hallwachs (1888); and by

Elster and Geitel (1889 and onwards), who in 1890 described a device consisting of an evacuated glass bulb with a positively charged anode and a cathode surface coated with an alkali-metal alloy or amalgam. This gave an electrical response when illuminated, and was the forerunner of the modern emission photocell.

Meanwhile Adams and Day¹ (1877) in Britain had generated an e.m.f. by illumination of a small annealed selenium bar held between platinum electrodes, and Fritts²⁴ (1884) in the U.S.A. had independently invented a cell, consisting of a metal base plate coated with, first, a thin layer of selenium and then with a transparent layer of gold, which altered its resistance in response to variation in illumination. This was the forerunner of the modern "barrier-layer" cell. It was used by Fritts and by Siemens⁴¹ (1885) to measure the intensity of daylight and as a microphone in telephony, but apart from a few further investigations made at about the same date, this type of cell appears to have been neglected for many years. From about 1930 onwards⁴¹ it was re-investigated and developed commercially, and the modern lowresistance cells which require no battery were produced. In the same period advances have been made in the design and use of the emission cell, largely owing to the stimulus of the sound film, picture telegraphy, and television.

PHOTOELECTRIC COLORIMETERS

As far back as 1911 a photoelectric colorimeter was invented8, but little further development of this type of instrument seems to have taken place for some years. From about 1917, however, interest began to grow in the use of photoelectric cells for photometric measurement of the candle-power of electric lamps. In 1915 Langmuir had greatly increased the efficiency of the electric lamp by his invention of the gas-filled bulb. The new possibilities thus opened up of increasing the illuminating power of lamps probably stimulated interest in the problem of accurate assessment of candle-power, and attention was directed to the use of emission photoelectric cell photometers for this purpose²⁵. By 1920 their use had been extended to the colorimetric measurement of hæmoglobin 80, and in the next decade photoelectric methods began to be more frequently proposed for measurement of the colour or turbidity of liquids and for pH determination and colorimetric titration e.g. 23,35,47,48 In 1927 Toussaint 73 described a trichromatic colorimeter in which the colour of liquids or solids could be analysed into three components by means of photoelectric cells and filters.

Photoelectric colorimeters may be divided into two classes, employing either one or two photoelectric cells respectively. The double-cell type, described by Gibson²⁵ in 1919, employs a second or compensating photoelectric cell, to enable variations in illumination to be neglected and to give improved sensitivity⁶⁵.

Most of the early workers employed emission photoelectric cells, but the use of early types of selenium cells in photometry was also reported in 1913⁵² and 1920⁶². With the development of the

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simple, robust, and reliable barrier-layer cells in the past two decades, a great extension in the use of photoelectric methods in colorimetry has taken place. By 1932 Lange⁴⁰ had introduced a commercial photoelectric colorimeter of the twocell type in Germany, and in 1936 the first model of the Hilger Spekker instrument appeared in this country4. In the past few years the variety of available commercial models has increased considerably. Most of these employ a series of colour filters for use in colour selection, but recently a type has been introduced in which any desired portion of the spectrum is selected by means of a diffractiongrating monochromator*, and the use of separate filters is thus eliminated. A return to the employment of emission cells has been made in the modern photoelectric spectrophotometers, which may also be employed as colorimeters.

Before a description of the instruments themselves is given, the simple optical laws which are the basis of all colorimetric analysis will be described.

The Laws of Colorimetry

LAMBERT'S LAW—Lambert's law may be stated thus—

Layers of equal thickness of the same substance transmit the same fraction of the incident light whatever its intensity may be.

Thus, if one-half of the light is transmitted by a layer 1 cm. thick, one-quarter will be transmitted by one 2 cm. thick, one-eighth by one of 3 cm., and so on. Expressed mathematically, this becomes—

$$I_{\mathbf{T}} = I_{\mathbf{0}} A^{-I} \tag{i}$$

 $(I_{\rm T} \text{ and } I_{\rm 0} \text{ are the intensities of the transmitted and incident light respectively, } A \text{ is a constant, and } l \text{ is the thickness of the absorbing layer).}$

BEER'S LAW—Beer's law expresses a similar relationship to Lambert's law between the transmission of a solution and its concentration—

$$I_{\mathrm{T}} = I_{\mathrm{0}}B^{-\mathrm{c}}$$
 (ii)

(B is a constant and c is the concentration of the solution).

It is important to note that both laws are strictly true only when observations are made with monochromatic light, though they may usually be applied satisfactorily in practical work with light which is not strictly monochromatic. Indeed, the discoverers themselves did not use strictly monochromatic light; Beer's illumination, for instance, was obtained by filtering the light of an oil lamp through red glass, which would have passed a fairly wide spectral band.

The two laws are commonly expressed in a combined form—

$$\frac{I_T}{I_0} = K^{\omega lc}$$
 (iii)

where K is a constant. In the simplest terms, this means that—

The absorption of light is proportional to the number of absorbing molecules in its path.

Recently, Sippel⁵⁰ has derived mathematically, from first principles, a general law of light absorption showing that deviations from Beer's law should always occur with increasing concentration of a solution.

OPTICAL DENSITY AND MOLAR EXTINCTION COEFFICIENT

Equation (iii) can, of course, be written in the form—

$$\log_{10} \frac{I_0}{I_n} = \epsilon lc$$
 (iv)

and in this form it serves as the basis of one of the fundamental terms used in colorimetry and spectrophotometry. The left-hand side of the expression is obviously proportional both to the thickness of the absorbing medium and to the concentration of the absorbing substance in it; it is thus most convenient for practical use, is widely employed, e.g. for the calibration scales of instruments, and is known as the optical density.

Another variant of equation (iii)-

$$\frac{I_{\rm T}}{I_0} = 10^{-\epsilon lc} \tag{v}$$

is also frequently used, ε being a convenient measure of the absorbing power of a given substance. It is known as the *molar extinction coefficient* or sometimes as the Bunsen–Roscoe coefficient.

An important corollary of the principles just described is that optical densities are additive. For instance, if light in passage through a coloured medium is reduced in intensity by an amount which represents a density of d, then twice and three times the original thickness of medium will have densities of 2d and 3d respectively. The same argument applies to mixtures of coloured substances in solution, provided no chemical reaction takes place between them. For example, if a coloured solution of density d_1 has dissolved in it another solute which would, alone, give a density d_2 , then the mixed solution will have a density $(d_1 + d_2)$. This is important in connection with the determination of coloured substances in mixed solution, described more fully below.

A clearer mental picture of the meaning of the above terms can be obtained when it is understood that solutions having densities of 1 and 2 transmit, respectively, 10% and 1% of the incident light. The molar extinction coefficient may also be expressed in more practical terms as the optical density of 1 cm. thickness of a solution containing 1 mole per litre or as the reciprocal of the thickness (in centimetres) of a solution containing 1 mole per litre which reduces the light to one-tenth of its original value, i.e. which has a density of 1.

Waveband Selection and the Use of Filters

Filters are used in all photoelectric colorimeters and in some visual types, to increase the sensitivity of the instrument. (In some instruments a monochromator is employed instead, but the principle is the same.) To understand the reason for their use it is necessary to study the light absorption curve of a dye.

A monochromator is a device, incorporating either prisms or a diffraction grating, to allow any desired waveband of the spectrum to be selected for use.

In Fig. 1 are shown typical absorption curves for a red dye. The optical density is plotted against wavelength for a series of solutions of different strengths. It will be observed that part of the

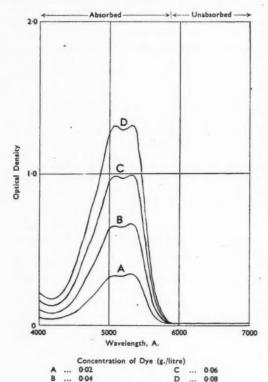


Fig. 1— Light Absorption of Aqueous Solutions of Azo Geranine 2GS (ICI)

spectrum—in this case the orange and red portions (6000–7000 A.)—is not absorbed at all, no matter what is the strength of the solution. In fact, we may say that the light passed through solutions of such

a dye consists partly of a component which varies in intensity in proportion to the concentration of the solution and partly of one which is invariable in intensity. This second part tends to reduce the variations in the other portion; and thus the changes in response of an instrument, when the dye concentration is varied, are less than they would be if the invariable portion of the light were removed.

It is, of course, a simple matter to remove it. All that is needed is a colour filter complementary to the colour of the dye solution, i.e. one which passes only the light which the dye absorbs and rejects the remainder of the spectrum. In the present instance this would be one with a green hue, but the argument applies to colouring matters of any shade. In practice it is not even necessary to know the character of the absorption curves of the solution or the filters available. All the available filters are tested with the given solution, and the one which gives the reading representing the highest light absorption is chosen for subsequent measurements.

VARIETIES OF FILTER

Filters, whether of dyed gelatin or glass coloured in the mass, never have a sharp cut-off, but may be chosen to pass either wide or narrow bands of the spectrum. Unfortunately, as the transmitted band is narrowed, the intensity of light is reduced, so that narrow-band filters can be used only with the more sensitive types of instrument. Fig. 2 shows the absorption curves of the red, green, and blue tricolour filters used with many photoelectric colorimeters. Fig. 3 shows those of a series of wide-band filters covering the spectrum more uniformly, and Fig. 4 shows the curves of the narrow-cut Ilford Spectrum filters.

During and since the recent war, a new type of filter has been developed³⁰. This operates by interference instead of by selective absorption. It consists of a thin glass base on which are deposited, by evaporation in a high vacuum, a partly transparent film of metal, then a film of a transparent

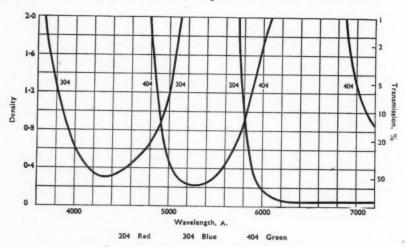


Fig. 2- Tricolour Filters (Ilford Ltd.)

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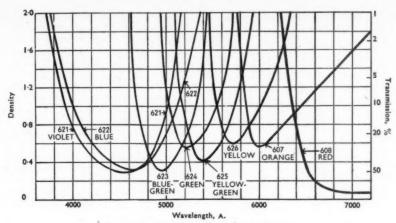


Fig. 3- Wide-band Filters (Ilford "Spectrum" Series)

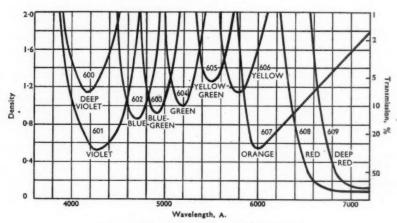


Fig. 4- Narrow-band Filters (Ilford "Spectrum" Series)

dielectric, and finally another partly transparent film of metal. The whole is protected by a cemented cover glass and is robust and durable. These filters have several advantages over the gelatin type—they are not subject to fading by light, they are unaffected by moisture, and they give a much higher light transmission relative to waveband width, or, alternatively, a narrower waveband for the same light transmission. The colour transmitted is governed by the thickness of the dielectric deposit, and the light transmission and band-width by the thickness of the metal deposit.

Fig. 5 shows typical transmission curves of such filters. They do not appear to have been used yet for routine colorimetric measurements, perhaps because they are at present considerably more expensive than gelatin filters and their properties are not widely known.

Some colorimeters may be used with a lamp giving a discharge in a gas or vapour, e.g. mercury vapour, and particular lines in the emission spectrum, including one in the near ultra-violet, may be selected by an appropriate filter. This gives

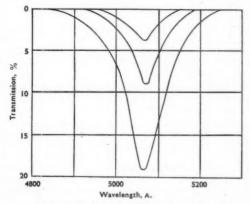


Fig. 5- Transmission Curves of Interference Filters

better results than gelatin filters, but the number of spectral lines which can be used is rather limited. The ultra-violet line is useful for work with some pale yellow or orange substances whose absorption bands fall partly outside the visual range²⁶.

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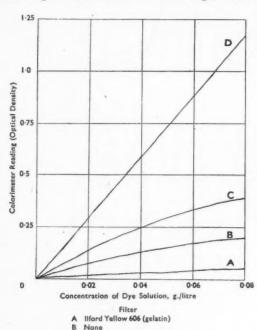
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LINEARITY OF RESPONSE WITH DIFFERENT FILTERS

If a series of coloured solutions of increasing strength is tested on a photoelectric colorimeter, each in turn with (i) no filter, (ii) an appropriate wide-band colour filter, (iii) an appropriate narrowband filter, the readings being plotted against concentration of solution, a series of curves like those shown in Fig. 6 is obtained. It will be observed from Fig. 6 and 7 that as the band of light used is



D liford Green 604 (gelatin)

Fig. 6— Influence of Filter on Photoelectric Colorimeter Readings for Azo Geranine 2GS Solutions

Chance Green OG I (all-glass)

narrowed, provided it is within the absorption band of the coloured solution, the curve becomes steeper, i.e. the instrument becomes more sensitive, for the reason already given. It will be seen, moreover, that the narrower the light band, the longer the straight portion of the curve (Fig. 7), and hence the wider the range over which the instrument can be used without previously being calibrated with a series of solutions of known strength. It follows that the simplest instrument to use should be one employing monochromatic light. But in the past, spectrophotometers were the only instruments of this type available, and they are costly and complex in construction. It has therefore been more usual to employ a simpler instrument with suitable colour filters.

The reason for the non-linearity of curves A, B, and C in Fig. 6 is that the instrument averages the transmissions over the wave-band, and not the densities, which are the units usually employed in measurement—

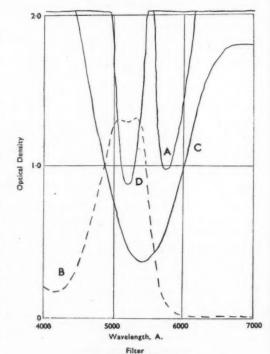
Consider two different wavelengths of the spectrum for which a given coloured solution shows

different densities of, say, 2 and 1 respectively. These correspond to transmissions of 1% and 10%, and hence the mean transmission recorded, if the instrument is equally sensitive to light of both wavelengths, is 5.5%, corresponding to a density of 1.26. If the concentration of the solution is doubled, the respective densities become 4 and 2, the transmissions 0.01% and 1%, and the mean transmission 0.505%. This corresponds to a transmission 0.505%. density of 2.30, which is less than a linearly proportional figure. With light which is not monochromatic, therefore, the curve of instrument response against concentration of solution tends to flatten at high light absorption values. Also, the more widely different are the transmissions at the different wavelengths, the less linear is the curve. This is the condition when a broad-band filter is used.

Apparatus for Visual Comparison

It follows from the Beer-Lambert laws that the relative strengths of two solutions of the same coloured substance may be compared quantitatively by varying relatively either their thickness or their concentration until they appear to the eye to be equal in colour strength.

On this basis a large number of types of apparatus, both simple and complex, have been developed. Two of the simplest are the well known Nessler tubes and Hehner cylinders. Both are in the form of vertical glass cylinders of equal



A liford Yellow 606 (gelatin)

B Azo Geranine 2GS (0-08 g./litre)

C Chance Green OG I (all-glass)

D liford Green 604 (gelatin)

Fig. 7— Absorption Curves of Filters and Dye

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bore, with bottoms ground flat. A standard solution is placed in one cylinder and the unknown in another, and their colour strengths are compared by viewing light transmitted directly upwards through the tubes.

With Nessler tubes comparison is made either by examining the standard against a series of equal volumes of solutions of the unknown of graded strengths, or by starting with solvent only in the comparison cylinder and adding aliquot portions of a stronger solution of the unknown, until a match is obtained. Hehner cylinders have draw-off cocks at the bottom and detailed volume gradations. One solution is run off until the two depths of liquid are a match in colour strength, when viewed directly from above.

If the test is one employing some standard colour, e.g. a reagent for a particular element or a pH indicator, it is often more convenient to avoid the preparation of a standard solution altogether, and to use instead a series of permanent glass colour standards. Such filters are now supplied in sets arranged in apertures round circular discs, and are employed in a simple apparatus in which the disc is rotated until a filter is found which agrees in strength with the test solution.

F

A ... Telescope

B ... Reflecting prisms

C ... Glass plungers

D ... Glass containers for liquid

E ... Vernier depth scales

Fig. 8- Dubosco Colorimeter

THE DUBOSCQ COLORIMETER

The Duboscq colorimeter incorporates a mechanical device to avoid manipulation of liquid and a simple optical system to facilitate viewing. It has been very widely used and has appeared in a large variety of designs of greater or lesser complexity for nearly a century, but is now being largely superseded by the photoelectric instruments.

Fig. 8 illustrates the principle of this instrument. Illumination is from below by a lamp or a mirror reflecting daylight. The light passes upwards through the two solutions, placed in glass cups, and then through two cylindrical glass plungers, which are inserted in the liquids, and through a pair of totally reflecting prisms, into the viewing The cups can be moved up and down by milled wheels (not shown), the depth of liquid under the plungers being indicated by the vernier scales. The glass surfaces at the bottom of the cups and plungers are ground optically flat. Matching to equal colour strength by moving one or other of the cups up or down is quite simple, because the two liquids are seen in the telescope as two contiguous halves of the field of view. It is obvious from a consideration of Beer's law that at the match point the ratio of strengths of the solutions is given by the inverse ratio of their depths*. By using two solutions of approximately equal strength any deviations from Beer's law may be neglected. In practice it is necessary to take a mean of several readings and to reverse the cups and repeat the readings, in order to compensate for possible unequal illumination and visual errors.

Duboscq instruments are simple, robust, and easily portable, and they do not require to be calibrated with a series of known solutions before use (though one known solution is always needed for comparison). In all these respects they show some advantage over the photoelectric instruments which are now largely displacing them. The principal disadvantages are their somewhat lower accuracy and the visual strain involved in their use for any extended period.

Instruments have been produced in which the intensity of light passing through a solution is varied by means of a movable glass wedge. This is inserted into a cell of coloured liquid, and thus the light path through the solution may be varied at will. For details of these and other types, the textbooks **.5.** **0,84** should be consulted.

HIGH-PRECISION VISUAL INSTRUMENTS

An early variation of the Duboscq principle was made by Patterson⁵⁰, who arranged a direct-vision spectroscope prism in the eyepiece of a Duboscq colorimeter and was able to determine dyes in solution quantitatively by equating the brightness of the absorption band in the two halves of the field; but it is only in comparatively recent years that more elaborate visual instruments have been produced commercially, mainly in Germany and the U.S.A.

In one German instrument (the Hellige colorimeter) the calculation was simplified by the device of moving the two cups simultaneously in opposite directions, by means of gears connected to a dial indicating directly the inverse ratio of their depths.

A number of precision colorimeters on the Duboscq principle were made by Leitz. These included the Absolute Colorimeter²⁹, developed by Thiel ^{38,69-71}, a remarkable feature of which was an aqueous solution of dyes giving a true neutral grey hue⁶⁶⁻⁶⁸, i.e. having the same optical density (0·5 at 1 cm. thickness) at all visual wavelengths. This was used in one side of the instrument in place of the normal standard solution. It enabled the colorimeter to be used also for the measurement of extinction coefficients and optical densities of solutions, or even, by the use of a series of filters mounted in the instrument, for plotting rough spectral absorption curves.

The Leitz neutral grey solution was composed of dyes, and its composition was not disclosed. Thomson⁷², however, has given details of the composition of a neutral grey solution prepared from inorganic salts.

Like the simpler Duboscq colorimeters, these precision instruments are being displaced by photoelectric apparatus, which is, however, not always of such a high standard of performance. Müller, one of the pioneers in the application of photoelectric technique to colorimetric measurement, says of these visual instruments⁴⁶: "To many their days seem to be numbered in view of photoelectric developments, but the best resources of the last half century's optical theory and practice have gone into their design and they are real instruments in a sense achieved by too few of their photoelectric successors."

The Photoelectric Cell

Photoelectric cells or photocells are devices by which light is made to produce an electric current varying in response to variations in the light intensity. They consist essentially of some sensitive

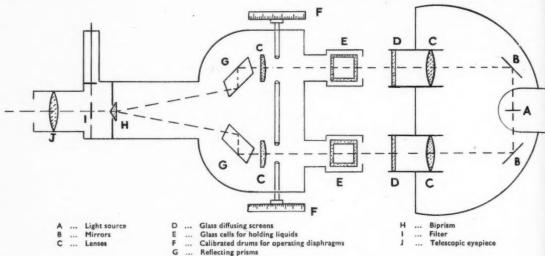


Fig. 9- Zeiss Pulfrich Photometer

Other precision instruments have been introduced by several makers, in which the intensity of light reaching the eyepiece through the two solutions for comparison is controlled either by a variable diaphragm, by an arrangement of fixed and rotating Nicol prisms, or by movable neutral wedges. These instruments are usually referred to as photometers, and they may be adapted for many uses, including the measurement of the gloss of surfaces, but they are equally suitable for the colorimetric analysis of liquids.

In the well known Zeiss Pulfrich photometer^{5,9,53} (Fig. 9) the solution for determination and the pure solvent are viewed in juxtaposition through a telescope by means of a system of prisms and lenses, the relative light intensities being matched by adjustment of iris diaphragms. Nine very narrow-band monochromatic filters are arranged so that any one can be inserted at will in the telescope. Cells from 1 mm. or less to 50 cm. or more may be used, and a wide range of accessories is available for adapting the instrument for many types of photometric work.

surface which emits electrons when light falls on it. Two general types are in use—

- (A) Emission cells
- (B) Barrier-layer or rectifier cells.

(A) THE EMISSION CELL

The emission cell consists of an anode and a lightsensitive cathode, in a glass bulb. The anode is a
metal rod or a wire grid and when in use is kept at
a positive potential. The cathode has a metal base,
which may be a silver plate or a silver mirror
deposited on the inner surface of the glass bulb.
Its light-sensitive surface consists usually of silver
oxide and caesium. This is produced by electrolysing the silver in an oxygen atmosphere in the
bulb, and then distilling caesium into the bulb,
from a heated side tube. The cell may finally be
evacuated or filled with an inert gas, e.g. argon or
helium. Greater sensitivity has recently been
obtained by the use of caesium-antimony or
caesium-bismuth cathodes.

The vacuum cell produces a current proportional to the light intensity. The gas-filled cell does not necessarily do so, but it has greater sensitivity. Consequently vacuum cells are used for measuring devices, and gas-filled cells are employed where detection of weak light intensities, and not their measurement, is necessary.

Emission cells, as already mentioned, require an applied potential, and on account of their high internal resistance they generate currents of very small magnitude. Consequently, thermionic amplifiers are necessary before they can be used to operate any measuring device.

(B) THE BARRIER-LAYER CELL

The barrier-layer cell is much simpler and more robust than the emission cell, and is used in almost all modern commercial colorimeters. It consists of a small, thin iron disc coated on one side, first with

A Metal base plate
B Salenium layer
G G Galvanometer

Fig. 10- Diagram of Barrier-layer Photoelectric Cell

a layer of selenium which has been annealed at a suitable temperature to give it the necessary photoelectric properties, and then with a protective and conducting layer of silver, gold, or platinum, which is so thin that it is transparent. This is applied by sputtering or condensation in a vacuum. A thin protective layer of lacquer covers the transparent metal layer. A thicker metal ring is deposited round the edge of the disc for electrical contact. Fig. 10 illustrates the principle of the cell. The coated side is exposed to the illumination, and light passes through the transparent metal coating, releasing electrons from the selenium. Selenium is a semi-conductor, but the released electrons are collected by the transparent metal layer immediately in contact with the illuminated sensitive surface and escape to the outer contact ring. Connections are made to a galvanometer by means of springs pressing on this ring and on the undersurface of the disc. A non-conducting or "barrier" layer, of the order of 5×10^{-6} cm. thick, is believed to lie between the selenium and the transparent metal layer41. Without it, no external current would be generated, because the cell would short-circuit itself internally. This is the origin of the name commonly given to these cells.

The value of barrier-layer cells lies in their ability to become, when illuminated, small sources of electric power, without need for amplification. They generate sufficient current to operate a galvanometer directly, without any external source of supply such as batteries or

amplifiers. They thus enable photoelectric instruments to be made small, compact, and simple. One of their familiar uses is in the pocket light exposure meters used by photographers, but they have many other uses in scientific instruments and are now widely employed in a variety of colorimeters.

Electrons are released from the selenium in direct proportion to the intensity of the illumination. Unfortunately, this does not necessarily mean that the current measured by the galvanometer is also in direct proportion to the light intensity. The reason is that the internal resistance of the selenium in the cell itself is not constant, but decreases with increase in light intensity. Since the internal resistance acts as a shunt across the cell terminals, the measured current shows an increasing departure from proportionality as the intensity of light

increases. This undesirable tendency can, of course, be reduced by making the cell resistance high in proportion to the external resistance, i.e. by using a low-resistance galvanometer, and in this way a linear response curve up to at least 4 ft.-candles is obtained, the output of the cell being of the order of 2 microamp. per ft.-candle. Except in special types of selenium cell, the internal resistance is too low for amplifying equipment to be employed.

Barrier-layer cells are not uniformly sensitive to the whole spectrum, but their spectral sensitivity curve (Fig. 11) is very similar to that of the human eye. The maximum is at about 5500 A., and falls by about 50% at 4000 A. and 6500 A. A characteristic fault is their liability to show fatigue effects. The current may drift

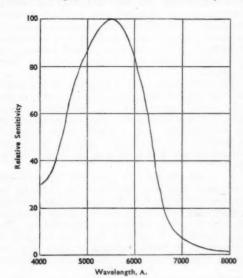


Fig. 11—Spectral Response Curve of Barrier-layer Cell (Evans Electroscienium Ltd.)

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downwards when the cell is first exposed, and it may require several minutes, sometimes even hours, to become steady. Consequently, it is advisable to switch on the light several minutes before readings are taken with a photoelectric colorimeter. They are, however, robust and are not damaged by excessive exposure to light if left on open circuit.

Photoelectric Colorimeters*

A great variety of designs of photoelectric colorimeters have been described. They may be divided broadly into two classes—the single-cell and double-cell types- and each type may employ either barrier-layer or emission cells. In the singlecell type, a lamp illuminates one photoelectric cell only, and the depth of colour of a liquid is determined by the change in photoelectric current when a glass vessel containing the liquid is interposed in the beam. Provision is made for the insertion of colour filters, and an adjustable shutter enables the light intensity reaching the cell to be varied at will (Fig. 12). Several early types of instrument worked on this principle 47,48,57, often with emission cells.

A disadvantage of the single-cell type is that, unless special precautions are taken, variation of voltage supply to the lamp causes inconsistency in the readings. This can be largely overcome, either by using a constant-voltage transformer on A.C. mains, or by using a low-power bulb and an accumulator of generous capacity. In the two-cell instrument, the difficulty is avoided by illuminating two photocells simultaneously with the same lamp (Fig. 13). They are connected in opposition across the terminals of the measuring instrument, which may thus be used for null readings, with improved stability. The greater sensitivity obtained enables filters with a narrower transmission band to be employed. Measurement of a coloured liquid is made by interposing it in the path of the light beam to one photocell, and then adjusting the current from the second photocell until a balance is again obtained. This adjustment is usually made by means of a neutral optical wedge or by a mechanical diaphragm, but the use of a variable resistance in the circuit from the control cell has been described79.

The electrical circuits of instruments employing barrier-layer cells are of the very simplest type and offer little opportunity for variation, though Wood^{64,83} has developed a more elaborate circuit for null readings with a single barrier-layer cell. A detailed description of a number of suitable circuits for use with such cells has been given by Müller44

A novel design of two-cell photoelectric instrument has been developed in Germany by Havemann^{31,63}; in this the lamp illuminates two frosted glass discs, which are used as the sources of illumination, thus eliminating a lens system. The photoelectric cell behind the test solution is arranged to be moved towards or away from the source of light along a threaded rod, by rotation of a calibrated dial. It is claimed that this arrangement, particularly the absence of lenses, gives improved stability and accuracy, since the whole area of the photocell surface is uniformly illuminated. The illuminant may be either a tungsten filament lamp or a mercury, sodium, or cadmium vapour lamp, appropriate filters being used to isolate particular lines of the spectrum. Various designs of optical cell can be used, including one with an attachment of mechanical stirrer and burette for photometric titrations.

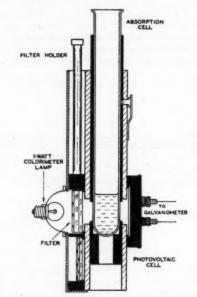


Fig. 12-Single-cell Photoelectric Colorimeter (Rubicon Co.)

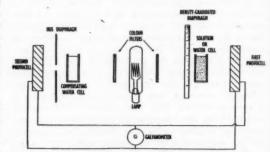


Fig. 13-Hilger Spekker Absorptiometer* EMISSION-CELL INSTRUMENTS

A large number of laboratory-constructed instruments employing emission cells have described, e.g. by Müller and Partridge^{47,48} and Andrews and Horecker³. These have usually employed thermionic amplification, but Withrow, Shrewsbury, and Kraybill⁸² avoided this by employing a bridge circuit and two photocells. Chamberlain¹³ gives constructional details of an instrument employing a beam of light, mechanically interrupted at audio-frequency before reaching

[•] Few details are given here, since these are readily available in the literature issued by the many British and American manufacturers. Continental types are described in some of the books and papers referred to ³¹, ³⁴, ³⁵, ³⁵.

This instrument has recently been redesigned, but the essential principles of operation shown here are unaltered.

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the photoelectric cell. The fluctuating current thus produced by the cell can be amplified by an A.C. amplifier, with the advantage of improved stability and absence of disturbances due to stray light reaching the cell. Davenport¹⁷ has used the same method in his continuous-reading apparatus, described more fully below. Chamberlain's instrument may be employed either for colorimetry, for gloss measurement, or even as a micrometer for determining fibre diameter.

Cunliffe¹⁶ has described the construction of a simple instrument employing an emission cell (Fig. 14). The need for a separate amplifier is avoided by connecting the photocell, when required, to a standard pH-meter; thus the expense and complication of construction are considerably reduced.

visible spectrum and even & little beyond the normal visual range at either end.

A much more elaborate development of this principle is seen in the modern photoelectric spectrophotometer12, which, though it may be used for colorimetric analysis, is principally intended for plotting absorption spectra.

Continuous-reading Colorimeters

Where rates of change of colour in liquids are required to be measured over a period of time, some form of continuous-reading colorimeter is desirable. Several laboratory-constructed designs are described in the literature, and a commercial device was marketed some years ago in Germany for this purpose.

The German Altmann colorimeter⁴¹ was designed

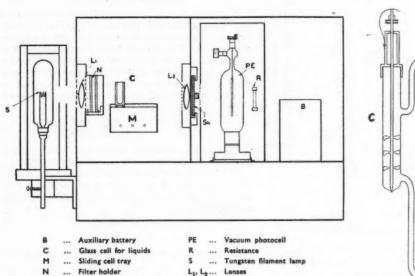
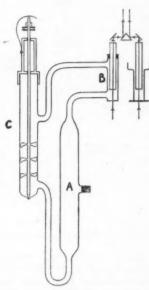


Fig. 14—Photoelectric Colorimeter employing Emission Cell (Cunliffe 16)

... Shutter



Apparatus for Determining Changes in Strength of Dyebath (Speakman and Smith)

INSTRUMENTS INCORPORATING A MONOCHROMATOR

A recent commercial development is the introduction of photoelectric colorimeters incorporating a monochromator in place of filters. In these a 6- or 12-volt lamp is used to form a spectrum by means of a slit and a diffraction grating. additional slit is located in the plane of the spectrum image, light from this slit illuminates the selenium photoelectric cell, and this in turn operates a mirror galvanometer. Thus, by rotating the grating by means of a dial calibrated in wavelengths the waveband falling on the cell can be changed at will and no filters are required in normal operation. A didymium filter is used, when desired, to check the wavelength scale. These instruments represent an advance in convenience and speed of operation over the types employing filters. They have the additional advantage of being suitable for plotting rough light absorption curves over the whole

for continuous measurement of e.g. water turbidity. The liquid passed, by side inlet and exit tubes, through a long cylinder with glass ends. A photoelectric cell was placed at one end of the cylinder and a lamp at the other. A compensating photoelectric cell, illuminated by the same lamp, and a galvanometer were incorporated, and the whole was arranged in a portable cabinet.

Speakman and Smith⁶¹ used the device shown diagrammatically in Fig. 15. A is a glass tube containing wool fibres, introduced through a stoppered side-tube; C is a glass tube fitted with a stainless steel propeller, and B represents a Duboscq colorimeter. A and C were immersed in a thermostat, and when the tubes were filled with dye liquor the liquid was propelled continuously through one of the tubes of the colorimeter, so that its colour strength could be measured at any desired time by adjusting the plungers in the usual way.

Davenport's continuous - reading apparatus

employs an emission photoelectric cell¹⁷ (Fig. 16). The dye liquor circulates through a tube containing the fibre, the whole dyeing unit being in the form of a U-tube, the two arms being connected between the upper parts of their limbs by another tube, of rectangular cross-section. This serves the double purpose of completing the circuit for the liquor flow and of acting as an optical cell. A beam of light modulated at audio-frequency passing through this tube falls on an emission photocell, and the impulses thus generated are amplified by a logarithmic amplifier and operate a galvanometer. This may be of the normal visual type, or a continuous-recording instrument may be used to trace automatically a permanent record of the change in colour strength of the solution in the U-tube.

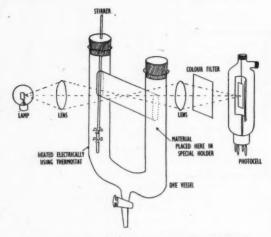


Fig. 16-Continuous Rate-of-dyeing Apparatus (Davenport)

Kienle, Royer, and McLeary36 and Royer, McLeary, and de Bruyne⁵⁵ have described a continuous-reading instrument consisting of two allglass parts, the dyebath chamber and the cell unit, connected together by an interchangeable groundglass joint. Several interchangeable cell units of various cell lengths may be used to suit the convenience of the experimenter. The essential features of the dyebath chamber are a reflux condenser and a side-arm for making additions to the bath. A coil of nichrome wire wound around the chamber enables it to be electrically heated. The cell unit consists of a mercury-filled thermoregulator for temperature control, a thin glass cell for the photometric measurements, a small tube near the top of the unit through which nitrogen gas is passed to circulate the liquid, and a draincock. The whole apparatus may be used with any suitable photoelectric measuring instrument, but Royer and his collaborators have actually employed a General Electric type of recording spectrophotometer.

Colorimetric Determination of Substances in Mixed Solutions

The use of colorimeters in organic, inorganic, and biological analysis and micro-analysis and for fluorimetry, nephelometry, and pH determination is well covered by numerous textbooks, but their use for analysis of mixed solutions has seldom been described*. By the choice of suitable filters a colorimeter may be used to determine coloured substances in mixed solution, provided, of course, that they do not interact chemically with each other. The procedure is as follows—

The individual substances present are first examined separately, and the appropriate filter is chosen for each. Then a density reading is obtained with a solution of known strength of each substance with its own appropriate filter and also with the filters chosen for the other component(s), in turn. Finally the sample solution of mixed substances is measured successively with each filter. Under these circumstances, as already explained, the densities of the individual substances are additive (p. 617).

TWO-COLOUR MIXTURES

For simplicity it is assumed that all measurements are made with the same depth of solution. Suppose a solution containing two coloured substances, A and B, present in concentrations $c_{\rm A}$ and $c_{\rm B}$ respectively, is measured at two wavelengths, λ_1 and λ_2 . Let the optical densities of the substances measured alone, at the same concentrations as they are present in the mixture, be respectively—

the k's being constants which are readily determinable by measurements on known solutions.

If d_1 and d_2 are the observed optical densities of the mixed solution at λ_1 and λ_2 respectively, then since the optical densities of the individual dyes are additive—

$$d_1 = k_{A1}c_A + k_{B1}c_B d_2 = k_{A2}c_A + k_{B2}c_B$$

Solving for $c_{\rm A}$ and $c_{\rm B}$, we obtain the expressions—

$$c_{\rm A} = \frac{k_{\rm Bg}d_{\rm 1} - k_{\rm B1}d_{\rm 2}}{k_{\rm A1}k_{\rm B3} - k_{\rm A2}k_{\rm B1}}$$

$$c_{\rm B} = \frac{k_{\rm A1}d_{\rm 3} - k_{\rm A2}d_{\rm 1}}{k_{\rm A1}k_{\rm B3} - k_{\rm A2}k_{\rm B1}}$$

Selling⁵⁶ has given the figures reproduced in Table I to illustrate his observed results for two dyes in mixed solution, determined in this manner, compared with the values calculated from measurements on the individual dyes.

The results are not always so reliable. Knudson, Meloche, and Juday³⁷ used a one-cell Evelyn photoelectric colorimeter to determine aluminium in presence of iron, with the hæmatoxylin reagent. Their results were accurate only to about \pm 5%. This low accuracy may have been due to lack of sharpness and inadequate separation in the absorption bands of the solutions or filters used, or both.

^{*} A description of the determination of coloured substances, alone and in two-colour mixtures, by examination of absorption curves with the spectrophotometer, was given by Weigert¹⁹.

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In the special case where the two absorption bands do not overlap at all, each filter, of course, gives a reading representing one coloured substance only, and no further calculations are involved. This sometimes occurs with compounds exhibiting two complementary colours.

MIXTURES OF MORE THAN TWO COLOURS

The method is theoretically applicable, of course, to more than two colours, and is limited only by the separation of the absorption bands and the sensitivity of the instrument. So far it does not appear to have been much used for determining three-colour mixtures, but in view of their wide-spread employment in dyeing practice and the present availability of colorimeters operating on narrow wavebands, including some in the ultra-violet region, the subject merits investigation. In such a case the three appropriate filters would be chosen and measurements of known solutions of the individual colouring matters and of the unknown solution made with each, as described for a two-colour mixture.

Suppose that the three substances, A, B, and C, are present in concentrations $c_{\rm A}$, $c_{\rm B}$, and $c_{\rm C}$ respectively, and that their optical densities alone with the three individual filters are given as before by expressions of the type $k_{\rm A1}c_{\rm A},\ldots k_{\rm C3}c_{\rm C}$ respectively. Then the optical density readings of the mixture with the three filters are—

$$\begin{aligned} d_1 &= k_{\rm A1} c_{\rm A} + k_{\rm B1} c_{\rm B} + k_{\rm C1} c_{\rm C} \\ d_2 &= k_{\rm A2} c_{\rm A} + k_{\rm P2} c_{\rm B} + k_{\rm C2} c_{\rm C} \\ d_3 &= k_{\rm A3} c_{\rm A} + k_{\rm B3} c_{\rm B} + k_{\rm C2} c_{\rm C} \end{aligned}$$

The solution of three such simultaneous equations is readily obtained by the use of determinants. The required concentration values are obtained by solution of the following determinants—

$$c_{A} = \begin{vmatrix} d_{1} & d_{2} & d_{3} \\ k_{B1} & k_{B3} & k_{B3} \\ k_{C1} & k_{C2} & k_{C3} \end{vmatrix} \div K$$

$$c_{B} = \begin{vmatrix} k_{A1} & k_{A3} & k_{A3} \\ d_{1} & d_{3} & d_{3} \\ k_{C1} & k_{C2} & k_{C3} \end{vmatrix} \div K$$

$$c_{C} = \begin{vmatrix} k_{A1} & k_{A3} & k_{A3} \\ k_{C1} & k_{C2} & k_{C3} \end{vmatrix}$$

$$d_{1} & d_{2} & d_{3} \end{vmatrix} \div K$$

$$d_{1} & d_{2} & d_{3} \end{vmatrix}$$

These expressions are expanded diagonally in the manner illustrated by the expansion of K—

$$K = k_{A1}k_{B3}k_{C3} - k_{A1}k_{B3}k_{C3} - k_{A2}k_{B1}k_{C3} + k_{A2}k_{B3}k_{C1} + k_{A3}k_{B1}k_{C3} - k_{A3}k_{B2}k_{C1}$$

The Accuracy of Colorimeters

A statistical investigation of the accuracy of three types of colorimeter was carried out by Davies, Giles, and Vickerstaff¹⁸. A standard commercial two-cell photoelectric colorimeter showed an overall mean standard error of 1.00% compared with 1.35% for a visual spectrophotometer and 2.49% for a direct - vision instrument of the Duboscq type. The last-named gave the least consistent results. Thus, a blue dye appeared to be most readily measured, and its mean standard error was 0.857%; but a yellow was difficult to measure and gave a figure of 5.47%. These figures may be compared with that of about 2% usually supposed to be the limit of difference between the strengths of dyed patterns detectable by an experienced colour matcher. Another interesting observation made in this investigation is that the visual instruments give the most accurate results only when operated by an experienced colour matcher, but the photoelectric instrument can be operated equally accurately by operators trained or untrained in colour matching.

Desirable Future Developments

Now that simple and reliable photoelectric colorimeters are on the market at an economic price, the visual type is being steadily displaced, and it seems likely to be little used in the future. The advantages it still possesses are that it requires no source of power, it is instantly available, it has no delicate parts, and with reasonable handling there is nothing to go wrong. There is still, nevertheless, scope for improvement in the photoelectric instruments, particularly in adaptability to a wider range of optical densities and in increased accuracy.

One difficulty with most absorptiometric colorimeters is that they operate successfully only at comparatively low optical densities, i.e. below about 1.5. This means that with intensely coloured substances such as dyes, the solutions have to be reduced to a strength between 10-4 and 10-5 % before they can be measured in the usual depths of cell employed (10-20 mm.). This involves one, and sometimes two, successive dilution operations for each original solution, because it is not desirable to propare such weak solutions by direct weighing. When a series of solutions are to be measured, the preparation of the liquids for test is thus a much more lengthy operation than the actual measurements on the instrument, and it is also, of course, an additional source of possible error. An alternative is the use of thin cells. Cells of short light-path down to a thickness of 0.25 mm. are commercially available, but even with these, some adjustment of strengths by dilution may be necessary. A variable micrometer cell is also produced for the spectrophotometer. This cell offers the great convenience of allowing the depth of solution to be varied continuously from zero to 0.5 mm. in steps of 0.01 mm. This cell, however, owing to its size, is not adaptable to any photoelectric colorimeter at present available. It is, moreover, an expensive item, and at least two cells would be required for colorimetric use, one being used as a blank. If a simple and economic means of varying the thickness of liquid were available, it would greatly simplify colorimetric analysis.

No extensive investigation of the relative accuracy of different types of photoelectric instrument has yet been made, but as already described, one of the most sensitive commercial instruments has an accuracy of the order of 1.0%. For many analytical operations this may be insufficient. It may be that more elaborate instruments, based on the emission cell, will be needed to achieve improved sensitivity. Müller46 believes that three recent developments will have a great effect on the future design of photoelectric colorimeters. These are—the electronic stabilisation of light sources, the introduction of multiplier-type photocells, and that of inverse feedback amplifiers of great stability. Whatever may be the future lines of development, it appears that increased accuracy can be obtained only with a sacrifice of simplicity and ease of operation.

Terminology

There is need for clarification of the terminology of the present subject. For example, the various instruments concerned have been described by different authors as colorimeters, absolute colorimeters, comparative colorimeters, colour comparators, filter photometers, absorptiometers, absorptiometers photometers, and abridged spectrophotometers.

The subject also overlaps to some extent with spectrophotometry, which includes quantitative measurements of colour and light absorption made with light split into a spectrum by a prism or grating device.

The term colorimeters has been used for instruments measuring tristimulus values of coloured substances, e.g. the Guild and Donaldson colorimeters, as well as for the type of apparatus described in the present paper, which, strictly speaking, should be named absorptiometers; but the more euphonious term colorimeter has the claim to acceptance because of longer usage and established custom. If this use is accepted, the tristimulus instruments can be differentiated by being named trichromatic colorimeters.

In view of this confusion, the publication committee of the *Analyst* set up a panel to define spectrophotometric terms and symbols. This panel issued a report in 1942²⁷, which includes the following recommended terms and comments—

SPECTROPHOTOMETER— An instrument by means of which the absorption of a sample may be measured at any wavelength in a specified spectral range.

ABSORPTIOMETER OR DENSITYMETER—An instrument for measuring the absorption of a sample in which "white" light or light of a chosen restricted spectral range is employed. When a series of restricted spectral ranges is used, the instrument becomes an "abridged spectrophotometer".

COLORIMETER— (a) In a strict sense, an instrument for measuring the colour of light.

(b) The term is applied to such instruments as the Duboscq, which are strictly "colour comparators", but usage must for the time being justify the retention of the name "colorimeter" for this type of instrument

until the significance of the term is more fully appreciated. Its extension to newer photoelectric instruments, which are really absorptiometers, is not justified by usage and is to be deprecated.

PHOTOMETER—A general name covering all instruments applied to the measurement or comparison of the intensity of light, e.g. the spectrophotometer, the Pulfrich instrument, etc.

Bibliography

The literature of the present subject is very extensive, and this review is intended only as a guide to its more important aspects.

Full accounts and illustrations of a wide variety of visual instruments are given in textbooks by Yoe⁸⁴ and Snell and Snell⁵⁰. Photoelectric apparatus is described and illustrated by the latter authors and by Willard, Merritt, and Dean⁸¹, and in very comprehensive papers by Müller^{44–46}, who also describes and illustrates several precision visual instruments.

The chemical methods of colorimetric analysis are described in numerous textbooks and monographs, e.g. those by Allport², Delory¹⁹, Haywood and Wood^{32a}, Vaughan⁷⁴, and Yoe⁸⁴. There is also a German textbook by Lange⁴². Waters⁷⁷ has reviewed the methods of colorimetric estimation of dyes in solution and on the fibre.

The textbooks by Campbell and Ritchie¹¹, Hughes and Du Bridge³³, Lange⁴¹, and Walker⁷⁶ are amongst the many which describe photoelectric phenomena and the principles of operation of photoelectric cells. Müller⁴⁴ has surveyed photoelectric methods in analytical chemistry and has given a detailed account of the physical and electrical principles employed; his paper includes a discussion of the amplifier circuits suitable for use with emission cells.

Finally, much detailed information is provided in the literature issued by the various manufacturers.

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 Wiley & Sons Inc. 1950)—This volume has been
 received aince the present paper was written (see
 review on p. 640). It contains descriptions of the
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 theoretical aspects of the determination of mixtures
 in solution (Stearns, Chapter 7).

The Estimation of Anionic Detergents in Solution by Hartley Titrations

KATHLEEN SWANSTON and R. C. PALMER

A quick method for the estimation of anionic detergents is given. It is a modification of Hartley and Runnicles' method, no indicator being used, and either cationic or anionic detergent can be used in the burette. The method is shown to be at least as accurate as other published methods and is quicker and more straightforward.

Several methods have been used for the determination of anionic surface-active materials in solution. They can be divided into four groups—(a) the titration methods of Hartley and Runnicles¹ and Preston², (b) the method, based upon the solubility of complexes formed between anionic detergent and methylene blue in organic solvents, of Jones³, (c) a combination of the titration and the colour complex methods used by Epton⁴ and Barr, Oliver, and Stubbings⁵, and (d) the gravimetric

method of Kling and Püschel⁶.

Preston followed the surface tension as cationic detergent was added to an anionic one, and at the end-point there was a sharp increase in surface tension. The method is, however, very sensitive to the presence of inorganic salts. The accuracy claimed in Jones's method, when the detergent-methylene blue complex is extracted with chloroform and the detergent concentration estimated colorimetrically, is 1%, but the estimation is quite a long procedure. The methods of Epton and Barr et al. for the determination of anionic detergents vary only in the When cationic estimation of their end-points. detergent is added to anionic detergent + methylene blue + chloroform, the colour is discharged from the chloroform to the aqueous layer. Epton's end-point occurs when the colour of both layers is the same, and Barr's when the colour is completely discharged into the aqueous layer. Epton's method is not suitable below a concentration of 0.003 m. Barr et al. have used their method and their bromophenol blue modification at 0.001 m., but these methods are not as easy as a straightforward titration. The old benzidine hydrochloride method of Kling and Püschel is neither quick nor very accurate; an insoluble benzidine salt of the alkyl $(> C_{10-12})$ sulphate is formed, dissolved in solvent, and titrated.

The quickest and most straightforward method, when doing a large number of determinations, is that of Hartley and Runnicles. They estimated the concentration of a cationic detergent in a solution by titration against an anionic one, using bromophenol blue as an adsorption indicator. They say that titrations can be done in a detergent concentration as low as 0.001 m. and also in the presence of electrolyte up to 0.5 N. The indicator is pure blue in the presence of a cationic detergent and purple in an anionic detergent. At the endpoint of the titration the paraffin-chain anion and cation form an insoluble complex; the colour changes from pure blue to purple and the solution shows a marked fluorescence. Hartley and Runnicles titrated the solution to a colour midway between blue and purple. They recommend using artificial light to view the solution. They used the method only with the anionic detergent in the burette. We wanted a quick, accurate method for the determination of anionic detergents. We have investigated Hartley titrations, to see whether the cationic detergent could be used in the burette, because this would be more convenient for titrating a series of anionic solutions, and to see with what accuracy such titrations can be carried out under different conditions.

One great advantage of being able to use the cationic detergent in the burette is that the burette does not need to be kept hot, but can be used at room temperature, because solutions of cetyl-pyridinium bromide and cetyltrimethylammonium chloride (and maybe other cationic detergents, but we have no information on this point) stay super-saturated for a few hours; whereas solutions of anionic detergents usually start crystallising out at once, necessitating a hot-water-jacketed burette.

This paper describes the titration of cationic and anionic detergents in the presence of salt and in the presence of chlorophenol red, used as an indicator when sodium carbonate in the detergent solution has been neutralised with hydrochloric acid. It shows that the cationic detergent can be used in the burette; that the titrations are best done without an indicator, that they can be done in salt concentrations as high as 0·1 N., and that they are not affected by the presence of chlorophenol red.

Experimental

The sets of experiments consisted of (a) titration of a cationic detergent against an anionic with different amounts (including zero) of bromophenol blue as indicator and in the presence of sodium chloride; (b) titration of the anionic against the cationic detergent in the absence of indicator and in the presence of sodium chloride; (c) titration of the cationic and anionic detergents against I.C.I. standards (see below). The experiments were The burette was carried out at about 50°c. jacketed with water at 60 ± 5°c., and the test tubes, in which the titrations were done, were warmed from time to time in a flame to about 50°c. (judged by hand).

MATERIALS

In the majority of the titrations the anionic detergent was sodium cetyl (approx.) sulphate, called AAI throughout this paper; and the cationic detergent was cetylpyridinium bromide (C.P.B.). The AAI was obtained in the laboratory by crystallising Lissapol C paste, once from water, once from acetone containing 7% water, and then from alcohol. The cetylpyridinium bromide was a sample made at W.I.R.A. from cetyl bromide (BDH) and pyridine. The other detergents used

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TABLE Titration No. 1 3 4 6 6 7 Indicator, ml. 0.1 0.01 Normality of NaCl... 1.0 0.1 0.01 AA1, mg./100 ml. ... C.P.B., M. × 10⁻⁸*... 34-5 35.0 33-2 33-3 33-3 33.3 0.966 0.966 1.00 1.00 1.00 1.00 0.958 0.958 Burette AA1 AA1 AA1 C.P.B. AA1 C.P.B. AAI C.P.B. AAI 1.94 1.95 1.94 1.94 1.93 1-96 1-98 1-96 Titration values, ml. 1.92 1.92 1.89 1.96 2·04 2·03 2.07 2.04 2.03 2.04 1.96 1.92 1.82 2·05 2·07 1.91 _ _ 2.060 Mean 1.897 1-900 1.964 2-040 1.940 1.787 1.964 2.037 Mol. wt. of AA1 342.0 338-8 339-6 343-7 343-1 342-2 308-8 341-3 341-5 * Mol. wt. of C.P.B. (WIRA) taken as 382.8

were—an anionic detergent called AA2 and prepared in the laboratory in the same way as AA1; and sodium cetyl sulphate (S.C.S.) and cetyl-pyridinium bromide kindly supplied by Messrs. Imperial Chemical Industries Ltd., which we used as standards. These materials are tabulated below.

The indicator solution was the one recommended by Hartley and Runnicles, a 0-0002 M. solution of bromophenol blue (0-134 g./litre) made just alkaline with ammonia. The sodium chloride, sodium carbonate, and hydrochloric acid used were AnalaR chemicals, and boiled distilled water was used in all solutions.

MOISTURE CONTENTS OF MATERIALS

Samples (a few hundred milligrams) of all the detergents used were put in a sulphuric acid desiccator and weighed daily to constant weight to find the moisture contents. The dried samples were then kept in the desiccator. The moisture contents as a percentage of the wet weight were—

Sodium cetyl (approx.) sulphate, AA1		***		0.3
Sodium cetyl (approx.) sulphate, AA2	***	***		0.25
Cetylpyridinium bromide, C.P.B. (ICI)	***	***	***	4.5
Cetylpyridinium bromide, C.P.B. (WIRA)	***	***	***	4.0
Sodium cetyl sulphate, S.C.S. (ICI)	***	***	***	3.2

METHOD

Two-millilitre samples were titrated each time, and during the titrations the solutions were warmed to 45–50°c. and shaken, as recommended by Hartley and Runnicles.

Results

Table I gives the conditions and values obtained when C.P.B. (W.I.R.A.) and AA1 are titrated against each other. The results are compared by calculating the molecular weight of AA1. The nine sets of experiments in the table show that either the cationic or anionic detergent can be successfully used in the burette. We found that the titrations are best done without an indicator. When an indicator is used, at or near the end-point two changes occur— (i) when the anionic compound is in the burette, the colour changes from blue to pink and the solution starts to fluoresce (or, when the cationic compound is in the burette, the colour changes from pink to blue and fluorescence ceases); and (ii) a flocculent precipitate comes down. These two changes (i) and (ii) do not occur simultaneously. We suggest the use of (ii) rather than (i) as the endpoint, because the colour changes are difficult to see and also because when maximum flocculation is used as the end-point a titration of anionic against cationic agrees to a few parts in a thousand with the reversed titration. The results given in columns 1 and 2 of Table I were obtained early in the work with indicator present, though the end-point was judged by maximum flocculation. All subsequent titrations were done without indicator and judged in this way. Titrations 7, 8, and 9 show that the titrations can be carried out in salt concentration as high as 0·1 N. but not in N. solutions.

One of the difficulties in titrating anionic or cationic detergents is to obtain pure compounds for use as primary standards. The chief impurities are neighbouring homologues. The molecular weight, which changes by about 4% from one homologue to the next, is a better discriminant than the carbon or hydrogen content, which changes by only about 2%. The best evidence of purity is therefore to be sought in the internal consistency of the titrations of the substances among themselves. First C.P.B. (ICI) was titrated against S.C.S. (ICI). This titration gives the ratio of the actual equivalent weights of these two substances. This ratio agreed to 1 part in 1000 with the ratio of the formula weights (384.2 and 344.3) of cetylpyridinium bromide and sodium cetyl sulphate. Therefore either both substances are pure or else they are both impure to the same In this work we have assumed that they are both pure because it would be an unlikely coincidence if they were both impure to the same extent. We have accordingly used C.P.B. (ICI) and S.C.S. (ICI) as primary standards.

AA1 and AA2 were titrated against C.P.B. (ICI), and their molecular weights were found to be 341·4 and 344·1 respectively. The molecular weight of C.P.B. (WIRA) was found to be 382·8 (from titration with S.C.S. (ICI)). Table II gives

TABLE II

Cationic Detergent	Theoretical M	Theoretical Mol. wt. Experimental Mol. wt. of Anionic Detergents						
used in Titration	Experimental	Mol. wt. or	Amonic Detergents					
	AA1	AA2	S.C.S. (ICI)					
C.P.B. (ICI)	1.000	1.000	1.001					
C.P.B. (WIRA)	1.001	1.000	1.000					
	Theoretical Mol.	Wt. used						
C16 H33 SO4 Na	. 344-3	AA1	341-4					
C14H23·NC5H5}Br	384.2	AA2	344-1					

the ratio of theoretical molecular weight to experimental molecular weight for the anionic detergents from titration with the primary standard C.P.B. (ICI) and the now secondary standard C.P.B. (WIRA); the theoretical molecular weights used are shown in the table. It will be seen that each ratio is unity to within 1 part in 1000. This means

that, if we take AA2 as having a molecular weight of 344.1 (i.e. we take this as almost pure) and we take AA1 as having a molecular weight of 341.4 (i.e. somewhat impure), then all the titrations agree with one another to 1 part in 1000.

Thus we may say that, using maximum flocculation as the end-point, an anionic detergent can be titrated against a cationic (i.e. cationic in the burette) in 0.001 m. concentration to an accuracy of at least 1 part in 300. Also (see columns 3 and 4 and columns 5 and 6 in Table I) the same solutions when interchanged between flask and burette give the same result to at least 1 part in 300. Further (see columns 8 and 9) the presence of 0.1 N. salt does not interfere with the titration to this order of accuracy, but N. salt does so (column 7). The above conclusions are based on the means of about five titrations.

The method therefore seems to be at least as accurate as other published methods, such as those involving methylene blue for example, and is much quicker and more convenient. It has the advantage

over Epton's method that the cationic solution, which remains supersaturated long enough to make a water-jacketed burette unnecessary, can be used in the burette.

The authors wish to thank Dr. A. B. D. Cassie, Director of Research, and the Council of the Wool Industries Research Association for permission to publish this paper. They are indebted also to Dr. F. F. Elsworth for preparing the C.P.B.

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The Sorption of Anionic Detergents by Wool

KATHLEEN SWANSTON and R. C. PALMER

The rates of sorption of sodium cetyl sulphate by wool at 50°c. under varying conditions of salt concentration and pH have been measured. A qualitative explanation of the results is given using the approximation that the concentrations of ions have their stoichiometric relationship (as in equilibrium

The sorption of soap by wool has been measured by King¹, but there is little information about the sorption of other detergents except that of Neville and Jeanson² for Gardinol CA and Igepon T and Aickin³ for sodium alkyl sulphates. King's results showed that base from the soap is sorbed more than the fatty acid. The amount of fatty acid sorbed decreased and the amount of alkali removed from the solution increased with increased concentration of soap. The reaction occurring appears to involve primarily the alkali in the solution. Neville and Jeanson measured the sorption of Gardinol and Igepon T and showed that it decreased with increasing pH. The sorption of Igepon T was very large in solutions more acid than pH 4, and that of Gardinol in solutions more acid than pH 6. Aickin measured sorption of sodium alkyl sulphates by wool in 48 hr. using different concentrations of detergent. His results showed that the rate of sorption increased with concentration until a critical concentration was reached. Beyond this there was a decrease to a minimum and then a very slow increase with increasing concentration. The critical concentration is that for micelle formation. which is evidence for the statement that it is the long-chain ions that are involved in sorption. Aickin points out that the sorption of synthetic detergents is of a different nature from the adsorption of soap: the long-chain ion from an anionic detergent goes into the wool fibre, whereas the longchain ion from soap is partly deposited on the outside of the fibre in the form of fatty acid, as Palmer4 had earlier found in washing with soap.

The combination of acids and bases with wool has been studied by Steinhardt, and Steinhardt, Fuggit, and Harris. They measured the affinities of a number of anions for wool, and give the following affinity constants at 25°c.-

> Octyl sulphate 360 0.00 Dodecyl sulphate ... 2600 *** Dodecylsulphonate 3200

Although the theory on which these figures were produced has been criticised by Gilbert and Rideal7, it is evident that the affinity is higher the larger the hydrophobic part of the molecule. In acid solution detergent anions, being colourless acid dyes, are strongly sorbed by wool; and their affinity is so great that they are sorbed by wool in alkaline solution, as shown later and by Neville and Jeanson, who obtained some sorption even in alkaline solution.

This paper describes the results of experiments on the rate of sorption of one detergent, which is sodium cetyl (approx.) sulphate, by wool at 50°c. under varying conditions of salt concentration and pH. It is found that when the solution is thoroughly stirred sorption takes place rapidly at first and then more slowly. It is also found that a striking phenomenon takes place when neutral wool containing some detergent is stirred in an alkaline solution containing detergent. The detergent initially in the wool comes out into the solution, and after about six minutes detergent starts to go back into the wool and continues to do so till the wool contains more than its initial amount. This effect can be explained qualitatively by means of the high affinity of the detergent anions for wool and the known acid-base combining properties of wool.

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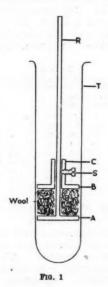
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Experimental

MATERIALS

Wool-Locks of Australian 64s were extracted with 40-60°c. petroleum ether for three hours, and were rinsed in water one by one. They were then made into a sliver as follows— The tip ends of each lock were combed by holding the lock by the root ends and pulling it repeatedly through a gill box faller (which is like a dog comb) held in a vice, beginning with the extreme tip and combing more of the lock at each pull. The lock was then turned round and the root end was similarly combed. Each lock was then drafted by hand to a wisp several times the original length, and these wisps were overlapped on the bench to make a rough sliver. This sliver was combed by passing six times through a machine called a gill box. By this means a well mixed sliver that is easy to handle and sample can be prepared from as little as 10 g. of wool. About 60 g. of wool was made into a sliver by the above method. This was extracted with (a) 40-60°c. petroleum ether, (b) anæsthetic ether, (c) absolute alcohol, (d) running tap water for 24 hr. Later a second lot of about 60 g. was prepared in the same way.



In some previous work some of the same wool prepared by extraction with (a) 40-60°c. petroleum ether, (b) water, (c) benzene and used in lock form gave irreproducible sorption results.

SURFACE - ACTIVE COMPOUNDS — The material used for sorption by the wool throughout the experiment was AA2 (see p. 631), which is sodium cetyl (approx.) sulphate. The titrant was a sample of cetylpyridinium bromide kindly supplied by Messrs. Imperial Chemical Industries Ltd. The

hydrochloric acid, sodium chloride, and sodium carbonate used were AnalaR chemicals. Laboratory distilled water that had been boiled was used throughout.

METHOD

A sample of sliver, usually weighing about 1.5 g., was made into a piston by compression between two perforated stainless steel plates A and B (Fig. 1). A is fixed to a stainless steel rod R; B can slide on R, and can be clamped to R by means of the stainless steel set-screw S, through the stainless steel collar C. The sliver is wrapped round the rod near the plate A; the rod and sliver are pushed into the glass tube T; the upper plate B is slipped on to the rod, forced down to compress the wool into a tightly fitting piston, and clamped. The wool piston is moved by hand gently up and down the tube, which contains the solution, and which is held in a water-bath at 50 ± 1°c. This procedure ensures very good stirring of the wool in the solution, because at every stroke almost all of the liquid flows through the plug. There is sufficient turbulence to stir in the small amount of inaccessible liquid in the rounded bottom of the tube.

Two sizes of piston apparatus as described above were used—the smaller, used for most of the experiments, viz. those involving a detergent concentration of 0-2 g./litre, was of 23 mm. internal diameter and 25 cm. long, and the larger was of 47 mm. internal diameter and 45 cm. long. The rates of stirring were such that a complete up-and-down stroke took about 4 sec. with the small apparatus and about 8 sec. with the big one.

In a sorption run a known weight of wool, always between the limits 1.47 and 1.53 g., is in this way stirred in 60 ml. (or 600 ml. for the big apparatus) of detergent solution; and 2-ml. (or 20-ml.) samples are pipetted out from time to time for determination of detergent, the method of determination being titration for 0.2 g./litre solutions and Jones's method for 0.02 g./litre solutions. The amount sorbed is calculated from these determinations and is expressed on the air-dry weight of wool. No correction is made for any change in concentration which would come about if the wool absorbed water not containing its proper proportion of dissolved substances, as this correction is Thus the amount of detergent negligible. apparently desorbed if 1.5 g. of wool at 16% regain becomes saturated by absorbing water containing no detergent from 60 ml. of a 0.2 g./litre solution of detergent (mol. wt. 344) is only 0.085 micromole per gram of wool, which is small compared with the amounts of detergent sorbed in this work, viz. of the order of 10 micromoles per gram of wool.

In the 0-2 g./litre experiment, the 2-ml. portions removed were titrated as described on p. 631. The initial solutions of AA2 and the aliquots were titrated with cetylpyridinium bromide (C.P.B.). Calculations of micromoles sorbed were made assuming that the molecular weight of C.P.B. was 385. The AA2 and C.P.B. were kept in a sulphuric acid desiccator.

In two of the experiments a more dilute detergent solution (0.02 g./litre) was used, and at this

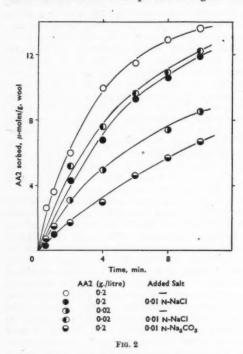
low concentration Hartley titrations are not satisfactory as the end-point is not clear. The colorimetric method of Jones⁸ was therefore employed, in which the acidified detergent solution is shaken with methylene blue and chloroform, whereupon a stoichiometric methylene blue–detergent complex goes into the chloroform and is estimated colorimetrically.

Results

In all the experiments wool (1.5 g.) prepared as described above was stirred in the piston apparatus in either 60 ml. of 0.2 g./litre (0.58 millimolar) or 600 ml. of 0.02 g./litre (0.058 millimolar) AA2.

DETERGENT ALONE

The amounts sorbed from both detergent solutions at different times are plotted in Fig. 2. Each



point is the mean of two independent determinations (i.e. beginning again with a new plug of wool). To give some idea of the reproducibility, the individual results are given in Table I. It will be seen that the reproducibility is better at the higher concentration, particularly at the beginning of the run. Table I also contains data for a single run of longer duration.

It will be seen from Fig. 2 that, as is to be expected, the amount sorbed from the 0.2 g./litre solution is at all times higher than from the 0.02 g./litre solution.

PRESENCE OF SALT

The results at the two concentrations in the presence of 0.01 N. sodium chloride are given in Fig. 2. The amount sorbed after 10 min. is about the same at both concentrations. At the higher

concentration sorption takes place more slowly at first, and a little faster later, than in the absence of salt, but the amount sorbed after 10 min. is not much different from what is sorbed in the absence of salt. At the lower concentration, sorption is faster than in the absence of salt, and after 10 min. the amount sorbed is 12·3 as compared with 8·5 micromoles per gram of wool in the absence of salt. Each point is the mean of two independent experiments. The reproducibility is about the same as with detergent only (Table I).

TABLE I Serption from AA2 alone

Time (min.)		0	2 g. AA	A2 sorb 2 per li	ed (μ-mole tre	s/g. wool) 0.02 g	. AA21	per litre
		1	2	3	Mean	1	2	Mean
0.5		2.6	2.6	-	2.6	-	-	_
1	***	3.8	3.4	-	3-6	_	-	-
2		6-4	5-6	_	6.0	4-9	2.9	3.9
4	***	10.0	9.8	-	9-9	6-6	5.2	5-9
6		12.0	11.0	-	11.5	8.5	_	_
8		12.8	13.4	-	12.9	7-6	7-8	7.7
10		13.4	13.8	-	13.6	8.8	8.9	8.8
30		-	-	18.7	18.7	-	-	-
60		-	-	23.0	23.0	_	-	-
90		-	-	24.5	24.5	_	-	_

PRESENCE OF SODIUM CARBONATE

Sorption experiments were carried out with a solution containing 0.2 g. AA2 per litre and 0.01 m. sodium carbonate. The aliquots were neutralised as described on p. 630 before titration with C.P.B. The amounts of detergent and alkali sorbed are given in Table II. The means of the four runs of this set are plotted in Fig. 2. The rate of sorption is much less than in the presence of sodium chloride of the same sodium ion concentration.

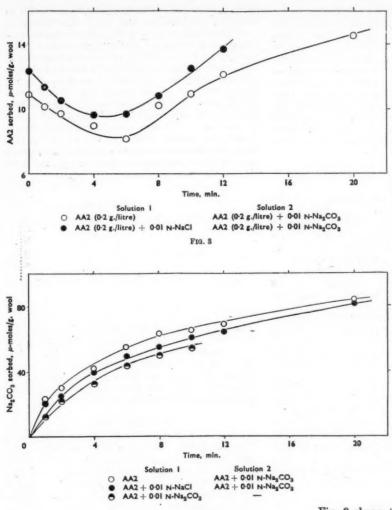
TABLE II Sorption from AA2 (0.2 g./litre) containing Sodium Carbonate (0.01 N.)

Time (min.)		AA2 sorbed $(\mu$ -moles/g. wool			ol)	Na ₂ CO ₃ sorbed (μ-equiv./g. wool)				ed vool)	
		1	2	3	4	Mean	- 1	2	3	4	Mean
0.5	***	0.2	0.8	1.0	0.8	0.70	4	10	12	0	6-5
1		1.8	1.8	1.4	1.2	1.55	4	20	20	4	12.0
2		0.6	2.4	2.4	1.4	1.70	16	34	30	4	21.0
4		3.2	3-4	3.2	2.0	2.95	34	40	38	18	32-5
6		5.0	4-6	4.2	3.6	4.60	42	48	48	38	44-0
8		6-4	5-6	5.8	5-0	5.70	48	54	56	42	50-0
10		$7 \cdot 2$	6-6	6.6	6-4	6.70	50	56	60	52	54-5

SORPTION BY WOOL ALREADY CONTAINING DETERGENT

In these experiments wool was allowed to sorb detergent from one solution and was then transferred to a second solution. The sorption or desorption of detergent from or into this second solution was studied. Altogether four kinds of experiments were carried out, the first solution being either (a) AA2 or (b) AA2 + 0.01 n-NaCl, and the second solution either (c) AA2 + 0.01 n-NaCl or (d) AA2 + 0.01 n-Na₂CO₃.

In these runs 1.5 g. of wool was stirred for 10 min. in a solution containing 0.2 g. of AA2 per litre with or without salt. A sample of this final solution was titrated, giving the amount of AA2 sorbed by the wool. The plug was pulled right out of the tube; the tube was rinsed; the plug was put back in the bottom of the tube (when once wetted, the



12

Solution 2 AA2 (0-2 g./litre) + 0-01 N-NaCl

AA2 (0-2 g./litre) + 0-01 N-NaCl

A suggested explanation of this ejection and resorption of detergent is given below, but to ensure that the effect is not a spurious one due to manipulation of the wool or changing the bath, we measured the sorption of detergent by wool already containing detergent from solutions of detergent and sodium chloride of the same sodium ion concentration as in the sodium carbonate experiments just referred to (Fig. 5). It will be seen that sorption from the second solution is, as expected, merely a continuation of the (incomplete) sorption from the first solution.

the water (usually about 3 ml.) held in the interstices of the plug. Fig. 3 shows that wool containing detergent (sorbed from solution either without salt or with salt), when put in an alkaline solution, for the first six minutes ejects detergent into the solution, and afterwards resorbs detergent in a quantity ultimately exceeding the quantity ejected. Fig. 4 shows the sorption of alkali from the solution, a process which is nearly completed after twenty minutes.

plug keeps its shape

when out of the tube

and can be put back

quite easily); the tube

was partly filled with

water; and the plug was

pulled up once through

this water to rinse it.

(That one pull through

the solution is enough

to replace all liquid in the plug by clean water can be shown by simple experiments with coloured solutions.) After

being thus rinsed, the

plug was weighed to give

the amount of water

carried over to the sec-

ond solution; it was

then put into the tube containing a second solution, and was stirred by pulling up and down in the solution as usual.

Aliquots were withdrawn and titrated from

time to time. The results

of these experiments are

given in Fig. 3-5. The

ordinates in Fig. 3 and

5 give the amount of

AA2 in the wool, that at

time 0 giving the amount

of detergent in the wool after the first treatment. The calculation of the

amount of detergent

sorbed is made after

making allowance for

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WOO

AA2 sorbed, p-moles/g.

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[Solution |

AA2 (0-2 g./litre) + 0-01 N-NaCl

AA2 (0-2 g./litre)

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EFFECT OF STORING THE WOOL

We had a good deal of difficulty at first in this work in getting reproducible results. Part at least of the cause of this was eventually traced to the effect of storing the wool between the preparing operation and the sorption experiments. Freshly prepared wool (up to about one week) takes up about 10 micromoles per gram in 10 min. from AA2 solution (0·2 g./litre). After storing for two months in a paper bag in the dark the wool sorbs 15–20 micromoles per gram. The reason for this is not known. All the results given above are from freshly prepared wool.

MIGRATION OF DETERGENT WITHIN THE WOOL

In the experiments using two successive solutions it is naturally important as far as possible to rinse the solution from between the wool fibres without desorbing detergent from within the fibres. This is why the rinsing technique described above was developed, for it is the minimum rinse that achieves replacement of the solution between the wool fibres.

If the wool is made to sorb detergent from AA2 (0.2 g./litre), is then thoroughly rinsed by pulling up in three changes of water and is finally stirred in AA2 solution (0.2 g./litre) containing 0.01 N. sodium carbonate, there is a small uptake of detergent (1-2 micromoles per gram) before the ejection and resorption. This is presumably due to the removal of detergent from the outermost layer of the fibre, so that the first thing that happens when this well rinsed wool is put in the second solution is the filling up of this outermost layer with detergent. If, on the other hand, the wool is rinsed thus, is left to dry overnight, and is then stirred in the detergent carbonate solution, this small initial sorption does not take place, but the ejection starts straight away just as with minimum-rinsed wool. This must mean that during drying detergent goes from the inside of the fibre towards the walls.

Discussion

The phenomena described in this paper are nonequilibrium phenomena, which are usually more complicated and difficult to interpret than equilibrium phenomena. We are concerned with the migration of ions-long-chain detergent anions, hydrogen ions, hydroxyl ions, and sodium ionsinto and out of the wool fibre. When the system is not in equilibrium the number of positive and negative ions in a particular element of volume averaged over a sufficient length of time to smooth out kinetic fluctuations will not in general be equal. One way of describing such systems would be to give the concentrations of positive and negative ions separately, e.g. of both sodium ions and chloride ions in the simple case of the diffusion of sodium chloride from a more concentrated to a more dilute solution. In systems whose physical size is as great as that of a wool fibre, however, the concentrations differ only very slightly7, and it is therefore a very good approximation to regard the concentrations of ions as having their ordinary stoichiometric relations (applicable to equilibrium systems) and to take account of the slight

inequality of positive and negative ions by introducing a new variable, viz. the electric potential.

A quantitative study of the diffusion phenomena described in this paper, which would be most easily carried out by considering the electric potential as a function of position and time in the wool fibre, is not attempted here. Instead, a simple qualitative explanation is offered using the (very good) approximation mentioned above, viz. that stoichiometric relations hold between the ions at all points in the system. It must be noted that the simple qualitative picture given below and the picture using the diffusion potential are merely alternative ways of describing the same phenomenon, and must lead to the same conclusions.

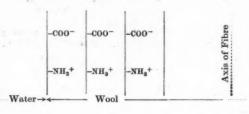


FIG. 6

Consider the wool fibre divided into cylindrical elements of volume having their common axis coincident with the axis of the fibre. Fig. 6 shows the first few of these elements of volume. We shall consider separately the diffusion phenomena that take place under different conditions, beginning with the simplest case.

DETERGENT ONLY

The ions in the solution are Na⁺ and Det⁻ (the detergent anion). The latter has a high affinity for wool, and therefore diffuses into the fibre from the solution. At the same time sodium ions also diffuse into the wool in equivalent amount to preserve stoichiometric neutrality. We may represent the diffusion reaction that occurs between the successive elements of Fig. 6 thus—

As the concentration of NaDet in the wool builds up, the net rate of sorption of NaDet decreases, because of the growing importance of the back diffusion reaction—

This is quite simple and straightforward.

On general chemical grounds one would not expect sodium ions to have any affinity for wool; and this is supported by the success of the Gilbert and Rideal theory of the combination of wool with acid in the presence of sodium chloride, in which this assumption is made? The sodium ions, then, are simply drawn in by the electrical attraction of the detergent ions.

DETERGENT PLUS SALT

The rates of sorption of detergent at two concentrations, 0.058 and 0.58 millimolar, each with and without 0.01 N. sodium chloride have been

measured: The more concentrated of these solutions will contain micelles, while the more dilute will not, as can be seen from the following argument— The detergent is approximately sodium cetyl sulphate. Lottermoser and Püschel⁹ give 0.59 millimolar, and Howell and Robinson¹⁰ give 0.51 millimolar, for the critical concentration for sodium cetyl sulphate at 50°c. The lower of the two concentrations we have used is well below the micelle point; moreover, the rough rule given by Palmer¹¹—

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$$[Na^{+}]^{0.5}[Det^{-}]_{c} = K$$

shows that micelles will probably not be formed in this solution even on the addition of 0-01 N-Na⁺. Taking the critical concentration [Det⁻]_c to be 0.55×10^{-3} in the absence of salt gives—

$$K = (0.55 \times 10^{-3})^{0.5}(0.55 \times 10^{-3}) = 13 \times 10^{-6}$$

With the addition of 0.01 N-NaCl we have— 0.010580.5 \times $C_{\rm c} = 13 \times 10^{-6}$

giving $C_{\rm c}=0.13\times10^{-3}$. The concentration used, 0.058×10^{-3} , is less than half this, and so, even allowing for considerable inaccuracy in the rule, we may safely say that the solution contains no micelles.

In the lower detergent concentration, 0.058 millimolar, i.e. in the absence of micelles, the effect of salt is to increase the rate of absorption of detergent. The diffusion process is—

and will presumably increase with the product of the ion concentrations, [Na+] [Det-]. An increase in [Na+] would therefore be expected to increase the rate of absorption; and this is what is observed experimentally.

The higher detergent concentration, 0.58 millimolar, is just around the micelle point. The effect of the salt addition will therefore be to cause a good part of the detergent anions to aggregate into micelles, with a consequent lowering of the number of single detergent anions: [Na+] is increased and [Det-] is decreased. To explain the observed decrease in rate of absorption we must suppose that the decrease in free detergent anions preponderates over the increase in sodium ions.

SORPTION BY WOOL ALREADY CONTAINING DETERGENT

When wool already containing detergent is put into a second bath containing detergent plus sodium carbonate, detergent comes out of the wool for about six minutes and then goes in again. This occurs only if the second bath is alkaline. In the experiments described here, the amount of detergent in the wool entering the second bath and the composition of the second bath are such that the wool will continue to take up detergent from the bath, as can be seen from Fig. 3, where (after the initial ejection) the wool continues to sorb more detergent than it originally contained. What requires explanation is the initial ejection of detergent into a solution from which the wool ultimately resorbs the detergent.

This can be simply explained on the qualitative

picture developed above. In the second solution in addition to the continuation of the sorption reaction—

$$Na^{+} \rightarrow Det^{-} \rightarrow$$
 (i)

there are two other possible diffusion processes-

$$OH^- \rightarrow \leftarrow Det^-$$
 (ii)

We may reasonably suppose that the rate of one of these processes increases with each of the following four factors—

- (a) and (b) the mobility of each anion
- (c) and (d) the gradient from water to wool of the activity of each ion.

(The activity of a single ionic species is a nonthermodynamic concept, but this need not prevent its use in discussing a non-equilibrium process like diffusion, which is outside the scope of thermodynamics.)

When the wool already containing detergent is put in the alkaline bath the chemical potential OH- is lower in the wool than in the solution. The chemical potential of Det- is also lower in the wool than in the solution (this is evident because the detergent eventually continues to go into the wool). Thus in process (ii) the OH- is going down a chemical slope and the Det- is going up a chemical slope. The direction of the process will therefore depend on the relative magnitudes of these two Now, when the wool already containing detergent is put in the alkaline second bath, the pH of the solution is about 11 and the wool, which has not been in alkali, is in equilibrium with a solution of pH about 5 or 6. The OH- ion is therefore going into the wool under a driving force of about 5 or 6 pH units, i.e. down a slope of 5 or 6 units of chemical potential. On the other hand, even if the amount of detergent in the wool at the beginning was so far from the equilibrium amount that it corresponded to an external detergent concentration of only 10-2 of the actual external concentration, the slope up which the Det- would go would be only 2 units of chemical potential. At first, therefore, process (ii) will proceed in a forward direction (OH- going into the wool, Det- coming out), and will later die away as the wool takes up alkali and the chemical slope for OH- ions becomes

Processes (i) and (iii) will proceed in a forward direction throughout.

Of the three ions, hydroxyl is fast and the other two are slow. We should therefore expect (ii) to be faster than (i) in the early stages, i.e. we should expect a net ejection of detergent, which is what is observed. Later, when (ii) (and incidently (iii)) have died away, (i) will predominate, and there will be a net uptake of detergent.

If the above qualitative picture is sound, then an interesting prediction can be made about different cations. According to this picture, if instead of sodium ions we use a slower moving cation, (i) should be slowed down, whereas (ii) should be unaffected. In this case the initial ejection of detergent should be more pronounced. This has been verified by using, among others, tetramethyl-

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ammonium as the cation, when the ejection of detergent proceeds both more quickly and further than with sodium. This is a useful confirmation of the theory. We hope to report more fully on the experiments with other cations in a later paper.

The authors would like to thank Miss Marion Dougill, who carried out some of the earlier experiments in connection with this work, and the Council of the Wool Industries Research Association for permission to publish this paper.

WOOL INDUSTRIES RESEARCH ASSOCIATION TORRIDON LEEDS 6

(Received 12th June 1950)

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 11 Palmer, R. C., Joint Discussion of Faraday Soc. and Soc. Chem. Phys. on Surface Chemistry (1949), p. 79.

CORRESPONDENCE

The Editor does not hold himself responsible for opinions expressed by correspondents

Mothproofing

The Editor SIR.

Reviewers are by custom allowed free expression of their opinions, but this licence does not extend to misstatement of fact in their reviews.

The review of my book, Mothproofing, includes the statement that—"To scientific workers engaged in work on the subject, the book may be of less interest, as it is based, not so much on first-hand knowledge, as on a patient study of the literature."

In fact, the book is largely based on my three years of practical mothproofing, including treatment of large-scale production with the best mothproofing agents available. Many people would consider that such experience affords a sounder basis for a technological book than that of having made innumerable and inconclusive experiments with small samples of wool; in particular it enables a balanced judgment to be offered to the finisher of the available proofing agents and methods.

Furthermore, if the reviewer does not consider that the description in the book of my glyoxal process for modifying the molecular structure of wool constitutes "first-hand knowledge", what can he mean by first-hand knowledge?

Naturally, part of the basis of the book is "a patient study of the literature", but this should in no way detract from, but rather add to, its interest to scientific workers.

I hope that you will publish this letter in your December 1950 issue and so mitigate the damage done to the book by the misleading statement in your review that the book was written without first-hand knowledge of the subject.

Yours faithfully

R. W. MONCRIEFF

3 CHURCH SQUARE HARBOGATE

30th November 1950

1 J.S.D.C., 66, 589 (Nov. 1950).

Notes

Meetings of Council and Committees November

Council-8th Publications—14th Colour Index Editorial Panel—6th Terms and Definitions-2nd Society's Medals—29th

Death of Member

We regret to report the loss by death of Mr. Luther Hartley.

George E. Holden, C.B.E., M.Sc., F.R.I.C. Honorary Member

At the meeting of Council held on 8th November 1950, it was unanimously resolved that Mr G. E. Holden, Immediate Past President, be made an honorary member of the Society, in recognition of his great services to the Society and to the dyemaking and dye-using industries.

Diplomas in Tinctorial Technology

Council has decided that it has become essential for the benefit of the industries and trades served by the Society that it should grant certificates and diplomas in tinctorial technology to properly qualified persons. To this end, the Diploma Committee has been instructed to prepare an examination system. Further details will be announced as soon as possible.

Review of Textile Progress Volume 1

This Review is being published jointly by the Textile Institute and the Society. Volume 1 relates particularly to the year 1949, and may be ordered direct from the Textile Institute, 16 St. Mary's Parsonage, Manchester 3, at £1 per copy, post free (orders should not be sent to the Society). There are twenty-four contributors to this first volume (342 pp. + Index), the subjects reviewed being as follows —

Introduction	***	***	***	***	***		G. S. J. White
Physics and C	hemist	ry of	Fibrous	Materia	als	***	B. Meredith
Cotton and Ce	llulose	- Ch	emistry				S. M. Neale
Physics of Wo	ol and	Silk	***	***			G. King
Wool and Silk	- Che	mistr	У	***			J. B. Speakman
Physics and C	hemist	ry of	Rayon	***			D. Entwistle
Physics and C	hemist	ry of	Bast Fil	res	***	***	H. J. Callow
Silk Production	n		***	***	***	***	F. O. Howitt
Wool Product	ion		***			***	A. B. Wildman
Fibre Product				ing Ka	pok)	***	E. Lord
Long Vegetab	le Fibr	es		***	***		A. J. Turner
Rayon	***		***		***	***	H. J. Hegan
Conversion of		into	Finished	Yarns	***		J. G. Martindale
Knitting	***	***	***				J. Chamberiain
Fabrica	***			***			J. Pollitt
Colouring Mat			***		***	***	J. Baddiley
Dyeing	***		844	200		***	H. A. Turner
Textile Printing		***	***	***	***	***	R. J. Hannay
Finishing Woo	l Fabr	ics	200				C. S. Whewell
Finishing		***		***			R. A. McFarlane
Analysis, Test						***	S. L. Anderson
Textile Micros	-		***				A. B. Wildman
Laundering as						***	F. C. Harwood
Mill Engineeri		***		***	***		H. Chamberlain

Association des Chimistes de l'Industrie Textile 23rd Congress, Lille 15-17th September 1950

The Society was officially represented at this function by Messrs. H. Blackshaw, J. Boulton, and E. A. Swift, who have stressed in their reports to Council the warmth of their welcome by their French colleagues and the excellence of the social arrangements. The Friday was devoted to works visits, while the Saturday included the A.G.M. of the A.C.I.T. and six papers, on the controlled scouring of wool (M. Robinet), physicochemical properties of degraded celluloses (Canon Pinte), effect of pH on the substantivity of dyes for cotton (C. Faure), etherified starch derivatives (F. A. Moeller), the chemistry of wool (M. van Overbecke), and photographic printing (R. Delattre). The Saturday concluded with a banquet and ball, and on the Sunday there were excursions to Bruges or Paris-Plage. Cordial greetings to the Society were formally extended by M. Rivat, President of the A.C.I.T.

Worshipful Company of Dyers

Dr C. J. T. Cronshaw, a past president and an honorary member of the Society, has recently been elected Prime Warden of the Company. The new Renter Warden is Mr. W. S. Leuchars.

Award of Olney Medal to Dr. G. L. Royer

The Olney Medal for 1950 has been awarded to Dr. G. L. Royer, Assistant Director of Application Research at the Calco Chemical Division of the American Cyanamid Co. The medallist's activities have been concerned mainly with the use of microscopy, spectrophotometry, and various physicochemical techniques in the application of dyes to textiles. He lectured to the London, Manchester, Midlands, Scottish, and West Riding Sections of the Society in 1947 (J.S.D.C., 63, 214, 254, 287 (1947)).

Dye Trade Census

According to Preliminary Report No. 67 onhe Census of Production 1948, published in the Board of Trade Journal (26th August 1950), the gross output of establishments (35–37) engaged in making intermediates, dyes, and tanning extracts rose in value (£ million) from 8·1 in 1935 to 23·1 in 1946 and 38·0 in 1948, the total number of persons employed averaging 8,174, 12,991, and 17,206 respectively.

American Dye Industry

Figures issued by the United States Tariff Commission indicate that output of dyes in the U.S.A. is falling, the total production in 1939, 1947, 1948, and 1949 being 120, 212, 201, and 139 million lb. respectively. The main classes of dyes produced in 1949 were azo (57·3 million lb.), anthraquinonoid and carbazole vat (26·9), indigoid and thioindigoid (17·5), and sulphur (17·5). The total output of lakes and toners was 37 million lb. The actual weight of dyes imported into the U.S.A. in 1949 was 771,000 lb., Switzerland supplying 97%, with minor quantities from the United Kingdom.

Dyes and Intermediates in Italy

According to Chimie & Industrie (64, 501 (October 1950)) the main Italian dyemaking plants are situated in the immediate neighbourhood of Milan. The annual consumption of primary materials (benzene, toluene, xylene, naphthalene, anthracene, and carbazole) totalled nearly 12,000 metric tons in 1949, though the plastics, pharmaceutical, etc. industries shared in this consumption. Annual production of intermediates was estimated at 25,000 metric tons, and that of dyes at 9000 metric tons. Italy was self-sufficient in intermediates, but imported 1500 metric tons of dyes, chiefly from the U.S.A. and Switzerland, with small quantities from Great Britain, Germany, and France. The 1948 rise in exports was not maintained in 1949, 3000 metric tons of intermediates and barely 1000 metric tons of dyes being sent to the Near and Far East, India, Latin America, etc.

Polish Dye Industry

It appears from an article by A. Metzner in Chemische Industrie (August 1950), quoted in Chemical Trade J. (127, 493 (1st September 1950)), that the output of dyes in Poland reached 3700 tons in 1949 compared with 1956 tons in 1938. Imports are increasing, their value in 1949 being DM 4·13 million, largely from West Germany. The three largest dyemaking firms are at Pabianice and Zgierz, near Lodz, and at Winnica, near Warsaw.

Dynel

Carbide & Carbon Chemicals Division of Union Carbide & Carbon Co., U.S.A., according to the Daily News Record (4th Aug. 1950), are not going to protect the word dynel as a trademark, but will use it as a generic term for fibres made from vinyl chloride-acrylonitrile copolymer. C. O. C.

Chemiefaser und Reyon

Germany is now following other countries in deprecating the use of the term "artificial silk". According to *Textil-Praxis* (5, 271–272 (May 1950))

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the Arbeitsgemeinschaft Kunstseide und Zellwolle-Industrie has changed its name to Industrie-vereinigung Chemiefaser, and has suggested that hence forth Chemiefaser be used as a general term for all man-made fibres. It is intended also to replace "Kunstseide" (artificial silk) by Reyon, which conserves the English pronunciation of "rayon" though the spelling is different.

Rainbow Sheep

Recent heavy floods in northern and north-west New South Wales have caused sheep to grow red, green, brown, and yellow wool, according to the Australian News and Information Bureau. It has been suggested that the discoloration has been caused by a by-product of bacteria active in regions with high summer rainfall.

New Books and Publications

Analytical Absorption Spectroscopy Absorptimetry and Colorimetry

Edited by M. G. Mellon. Pp. vii + 618. New York: John Wiley & Sons Inc.; London: Chapman & Hall Ltd. 1950. Price, cloth,

\$9.00 or 72s. 0d:

The appearance of this volume, which is claimed to be "the first comprehensive study of the fundamentals, methods, and apparatus involved in the analytical application of the absorption of radiant energy in the ultra-violet, visible, and infra-red spectral regions", is a sign of the growing importance of such methods in qualitative and quantitative analysis and in the determination of the structure of organic compounds. It will prove invaluable as a work of reference for all who have any interest in this field. Like many American textbooks of recent years, it is a co-operative effort by a team of authors. While this ensures that each aspect of the subject is dealt with by a specialist, the result is a series of individual monographs rather than a single volume with the uniform impress of a single mind, and there is some overlapping between different chapters. Though these faults may be regretted, they are, perhaps, almost inevitable with the continued expansion of research in this field and the increased specialisation which this entails. The separate chapters may be discussed briefly in order as follows-

1. CHEMISTRY: PREPARATION OF SYSTEMS FOR ABSORPTIMETRIC MEASUREMENT, by M. L. Moss (77 pp.)— This gives a general review of methods involving colour-forming reagents, both organic and inorganic, for preparing solutions for

colorimetric analysis.

2. Physics: General Principles of Absorptimetric Measurements, by M. G. Mellon (38 pp.)—The physical laws of light absorption and their validity or non-validity in particular cases are described.

3. Color Comparimeters by W. B. Fortune (45 pp.)—This includes descriptions of methods and apparatus employed in the visual comparison of coloured liquids, e.g. in pH determination, with either standard coloured solutions or fixed glass standards.

4. FILTER PHOTOMETERS by R. H. Müller (25 pp.)—This describes visual and photoelectric absorptiometers, including their basic principles of operation and, in the latter case, numerous electric circuits.

5. SPECTROPHOTOMETERS: ULTRAVIOLET AND VISIBLE REGIONS by K. S. Gibson (82 pp.)—This

gives both theoretical and practical descriptions of commercial instruments and their methods of use.

6. Photographic Methods by E. R. Holiday (38 pp.)—The principles and instrumental technique of the photographic recording of spectra are described.

7. APPLICATIONS OF ULTRAVIOLET AND VISIBLE SPECTROPHOTOMETRIC DATA by E. I. Stearns (133 pp.)— This chapter will be of particular interest to readers of this *Journal*, describing, as it does in a very thorough manner, the theory and practice of the qualitative and quantitative analysis of coloured substances, particularly dyes, in solution, both singly and in multi-component mixtures.

8. Spectrophotometers: Infrared Region by L. J. Brady (76 pp.) —A description of the use of infrared spectrophotometry in structural analysis, with diagrams and photographic illustrations of

modern apparatus.

9. Measurement and Specification of Color by D. B. Judd (86 pp.)—While this chapter, in itself, is an excellent survey of the theory and practice of trichromatic colorimetry, it is closely similar in content to the same author's recent monograph (reviewed below) and, dealing thus with a subject so far removed from the main interest of the present volume, its inclusion here appears unnecessary.

The standards of printing and illustration, paper and binding in this volume are excellent.

C. H. GILES

Colorimetry N.B.S. Circular 478

By D. B. Judd. Pp. iii + 56, with 34 Fig. Washington D.C.: United States Department of Commerce, National Bureau of Standards.

1950. Price, paper, 30 cents.

While the study and practical employment of methods for the exact physical specification of colour has grown steadily over the past twenty to thirty years, and has indeed become a well defined and specialised branch of physics, few convenient textbooks are available for those who wish to understand the basic principles and the practice involved. The present publication, while officially described as a "Circular", is in effect a small textbook, selling at a remarkably low price, yet well produced, clearly written, though in a rather condensed style, and generously documented with references to original sources (there are 144 literature references). The theoretical treatment covers

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the subjects of standard illuminants and observers, and the development of the best known co-ordinate systems of trichromatic colour specification. Descriptions are then given of trichromatic colorimeters and of the several systems of colour standards used for describing coloured samples, e.g. the transparent standards, represented by Lovibond glasses and Arny solutions; and by the systems employing classified arrangements of coloured surfaces, e.g. the Ostwald, Munsell, and Maerz and Paul albums. There follow descriptions of the use of such systems for the commercial control of the colour of products such as oils and pigments.

This publication should be in the hands of all who are concerned with exact colour measurement.

C. H. GILES

Ramie

Kultur, Verarbeitung, Eigenschaften und Verwendung By B. Luniak. Pp. 78. Zürich: Verlag Leemann, 1949. Price, 15.60 Swiss francs.

In addition to those vegetable fibres in common everyday use, considerable numbers exist which have, for a variety of reasons, failed to reach industrial significance. Every now and then, one or other of these minor vegetable fibres is "discovered" anew, and attempts are made to cultivate and utilise them, but few of these have stood the test of time. For too long, perhaps, ramie has remained within this shadow, and has tended to be looked upon as somewhat of a mystery fibre. Unfortunately, much of the literature pertinent to it has only too often served to enhance this feeling, for it is indeed depressing to read so often, in textbooks and publications of repute, statements not only unsupported by careful scientific investigation but often quite erroneous. Under such circumstances, therefore, this book with its well authenticated data coupled with so sound and practical an outlook is most welcome and is assured of high esteem in the field of textile technology.

It is difficult, however, to accept a number of the author's statements, especially those concerned with the future of ramie. It does not seem possible that mere modern improvements in fibre extraction, unspecified by the author in any detail, can alter the fact that ramie is a fibre most difficult to "win" in comparison with those at present in major commercial use. It is a pity also that the author has not dealt more fully with the chemistry of the degumming process in order to clarify the unnecessary obscurity with which this subject is commonly clothed. It is also not possible to accept, without presentation of much more precise analytical detail, Luniak's suggestion that ramie is more resistant to rot than cotton, hemp, etc.

Utilisation of ramie for such articles as bed sheets, table cloths, hand towels, kitchen cloths, aprons, coarse shirtings, carpet backings, curtains, upholstery, sail cloth, tent ducks, canvases, filter and press cloths, webbing, nets, ropes, sewing twines, etc. may indeed be feasible, but such structures can be equally well made with other, more accessible, fibres. It is difficult to visualise what particular attributes ramie possesses in such degree that expense becomes a secondary consideration. It is, therefore, unfortunate that the author has given us no detailed analysis of ramie economics in comparison with the major vegetable fibres of commerce.

In spite of these critical remarks, the book is worthy of very high praise and its author deserving of our warmest thanks for the undeniable merit of his work. The subject matter is written in a clear logical style and is well classified into a number of sections. These deal with the history, botany, and agricultural economy of the plant, the separation and properties of the fibre, spinning and weaving and the properties of yarns, fabrics, and ropes, whilst a final section deals briefly with a survey of the end uses for which ramie has been found suitable. The text is illustrated with many tables and graphs and also with photographs of undoubted excellence. Well printed and well bound, it is a valuable contribution to textile literature and should serve as the ramie reference book for a long time to come. It is to be hoped that an English translation may soon be forthcoming.

H. L. PARSONS

Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes.

Any publication abstracted may be referred to by members of the Society on application to

Dr. C. B. Stevens, Dyeing Department, Leeds University

Allied Colloids (Bradford) Ltd.

ACID DYESTUFFS ON WOOL PIECE GOODS—This pattern book is issued by the Société Anonyme de Matières Colorantes et Produits Chimiques Francolor and contains dyeings of 211 acid dyes illustrated in two, or more frequently three, depths. The dyes are classified in five groups—(1) good levelling dyes, (2) fast-to-light good levelling dyes, (3) Supracid dyes, (4) dyes with moderate level dyeing properties, and (5) dyes with high affinity. The optimum and alternative dyeing methods and all relevant fastness data are appended alongside each set of dyeings.

ALBIGEN A— This non-ionic auxiliary product, produced by the Badische Anilin- & Soda-Fabrik (B.A.S.F.), Ludwigshafen, is designed as an assistant in stripping dyeings and prints, particularly those produced with vat dyes. The card contains patterns illustrating the stripping and lightening action of the product on two vat dyes,

a sulphur dye, and a direct dye, and also its effectiveness in clearing the whites obtained by discharging a direct print.

CELLITON DYESTUFFS PRINTED ON ACETATE—Messrs. Allied Colloids (Bradford) Ltd. have issued a card illustrating a range of thirty-two dispersed acetate rayon dyes from the Celliton and Celliton Discharge ranges of the B.A.S.F. Printing recipes and fastness data are included in the text.

Indanthren Dyes— Under the title Notes on Selected Members of the B.A.S.F. Indanthren Range, Messrs. Allied Colloids (Bradford) Ltd. have issued seventeen cards, each of which details the more important features of either a particular Indanthren dye or two related ones and includes dyeings on cotton cloth. The relevant fastness data are given in each card, and a summary of instructions for preparing the stock vat and of the various dyeing methods is included.

INDANTHREN OLIVE MW- This vat dye, introduced by the B.A.S.F., is suitable for dyeing all forms of cellulosic material, preferably by the IN method. Recommended uses for it, alone or in mixtures, include the production of a variety of beiges and khakis on furnishing and awning material, and yarn to be subsequently bleached in the piece. It may also be applied by the pigment-padding method, and is of some interest on silk. Some fastness grades on cotton include-Light 8, soda boiling 4,

PALATINE FAST DYES ON LOOSE WOOL- This card, issued by the B.A.S.F., contains forty-eight self and mixture dyeings using a full range of Palatine Fast Dyes, With the exception of the two blacks, the recommended dyebath additions are 2-3% Palatine Fast Salt O and 5-6% sulphuric acid; if the former is omitted, the sulphuric acid should be increased to 8% at 30:1 liquor: material ratio, and to 11% if the ratio is increased to

PALATINE FAST DYES ON SLUBBING-This card, which is a companion to the previous one, contains forty self and mixture dyeings on wool slubbing.

Clayton Aniline Co. Ltd.
CHLORANTINE FAST NAVY BLUE BLL— This direct dye is the first in the Chlorantine Fast range yielding navy blues of good fastness to light. It is recommended for dyeing dress fabrics and furnishings, dyeings being unaffected by crease-resist finishing. It will produce solid dyeings on cotton-viscose rayon union material, and is preferentially absorbed by cellulosic fibres in unions with wool under all conditions. Acetate rayon is slightly stained. Dyeings are not dischargeable. Some fastness grades on cotton include— Light 7, washing at 50°c (soap and soda) 2.

CIBACET BRILLIANT BLUE BG NEW-This dispersed dye gives very bright blues on acetate rayon and nylon and is recommended for use alone and in mixtures on a variety of materials. Cellulose fibres are slightly stained, but this may be removed by a permanganate-bisulphite treatment. Dyeings on acetate rayon and nylon are not dischargeable, but direct prints can be produced on both fibres. Some fastness grades on acetate rayon include—Light 4, washing 4-5, water 4.

COPRANTINE RUBINE RLL-This direct dye yields bluish reds of good fastness to light and wet treatments when aftertreated on the fibre with Coprantine Salt II. Crease-resist treatment improves the fastness to light of the dyeings, while the hue is only slightly affected. It is recommended for furnishings and dress and knitted fabrics, and is also suitable for direct but not discharge printing. Some fastness grades on viscose rayon include— Light 7, washing at 80°c. 3-4, perspiration 4. FALL 1950 — This card contains forty dyeings on wool

cloth reproducing the fashion shades forecast by the Textile Color Card Association of the United States Inc.

Equalising acid and Neolan dyes have been used. FASHION SHADES— This card contains thirty-two dyeings to match the British Colour Council colours for wool B 1145-B 1176. The wool cloth used contains coloured cotton effect threads, and Neolan dyes have been employed.

FASTNESS PROPERTIES OF CHROME DYES ON WOOL-This booklet contains fastness data for dyeings on wool of the complete range of chrome dyes. The testing pro-cedures followed, full details of which are appended, are those given in the Second Report of the Society's Fastness Tests Committee. When more than one method of dyeing is suitable, fastness data for dyeings produced by each method are given.

KNITWEAR—This card contains twelve dyeings on wool yarn to match the colours No. K 200-K 211 sponsored by the British Colour Council.

KNITWEAR—Twelve dyeings on wool yarn are shown in this card. They are reproductions of colours No. K 212-K 223, suggested by the British Colour Council for Spring and Summer 1951.

NEOLAN PINK BE—This premetallised dye yields bright bluish reds. Dyeings are faster to light than those produced with Neolan Pink B or even with the BA brand, and, unlike the older dyes, the new product will build up to full reds. It is recommended for use on a variety of wool and weighted and unweighted silk materials, and is of interest for direct printing on both fibres. Dyeings are not dischargeable. Some fastness grades on wool include-

Light 5-6, milling 3-4, perspiration 5.

SYNCHBOMATE NAVY BLUE B— This chrome dye is recommended for dyeing by the single-bath method to give medium to navy blues on loose wool, slubbing, yarn, and piece goods. Dyeings have good fastness to wet treatments, light, carbonising, and chlorine. Some fastness grades on wool when applied by the Synchromate

method include—Light 6, carbonising 5, chlorine 5.
WOOL BLUE BF— This level-dyeing acid dye is recommended as a basis for blues and navy blues on yarn, piece goods, and wool felt. It does not stain cellulosic and acetate effect threads, and may also be used for shading chrome dyes, as it is unaffected by acid solutions of dichromates. Some fastness grades include— Light 3, washing 3, perspiration 3-4.

Geigy Co. Ltd
CUPBOPHENYL YELLOW BROWN RGL—This Class C
direct dye yields yellowish browns of good fastness to light and wet treatments when aftertreated on the fibre with copper salts. It is suitable for dyeing all forms of cellulosic material, particularly for crease-resist styles. Dyeings are not dischargeable. Some fastness grades on cotton

include— Light 6, washing at 60°C. 4, perspiration 4.
DIPHENYL BRILLIANT GREEN 5 GW— This Class B direct dye yields bright yellowish greens, which can be discharged to white under both neutral and alkaline con-It is suitable for dyeing all forms of cellulosic material, and is particularly recommended for use with Diphenyl Fast Yellow 3GL or Solophenyl Blue Green BL to produce bright green grounds for white and coloured discharges. Some fastness grades on cotton include—Light 3, washing at 40° c. 4, perspiration 4.

Sandoz Products Ltd.
ALIZABINE CHROME GREY BS— This chrome dve is recommended for use in mixtures, and may be applied by the on-chrome, afterchrome, and single-bath methods, although the Metomega Chrome Greys are more suitable for dyeing by the last method. It is suitable for use on wool at all stages of manufacture, the hue is relatively unaffected by metals, and cellulosic fibres are reserved when the afterchrome method is used. Some fastness grades of dyeings produced by the afterchrome method include—Light 5, milling 5, potting 4.

ARTISIL DIRECT COLOURS—This pattern book contains

dyeings of thirty dispersed dyes, twenty-eight of which are illustrated in three depths of shade. In addition to the usual dyeing instructions, lists of Lumicrease, Solar, Cuprofix, and level-dyeing acid dyes which reserve acetate rayon are also given for use when dyeing union fabrics. Details of the relevant fastness properties and the degree of staining of other fibres are appended alongside each set

ARTISIL DIRECT BLUE BSQ conc .- This dispersed dye gives very bright pure blues on both acetate rayon and nylon, the hue on both fibres being almost identical, as is also the case when it is used with Artisil Direct Yellow 2GN for greens. It is level dyeing and has good building-up properties. Cellulosic fibres are reserved. Dyeings are not dischargeable. Some fastness grades on acetate rayon

not dischargeane. Some assures grades on decay and include—Light 4, washing 4-5, perspiration 4.

AZO RUBINOLE 2GA, XYLENE LIGHT YELLOW 2G, and ALIZARINE LIGHT BLUE FPA CONC.—These three level-dyeing acid dyes are recommended for producing economically mixture dyeings of good, balanced fastness to light on hosiery yarn. The card contains dyeings of each dye in hosiery yarn. Fashion Shades—This card contains thirty-two

dyeings on wool cloth to match the wool colours B 1145-B 1176 of the British Colour Council, and a further twelve on yarn reproducing the Knitwear range K 200-K 211, both ranges being approved for Autumn and Winter 1950.

LUMICREASE BLUE L, BLUE GL, and SKY BLUE 4GL— These direct dyes are further additions to the range of dyes specially recommended for dyeing materials which are to be crease-resisted by the normal urea-formaldehyde method. The light fastness of dyeings of the Blue L and GL is unaffected, while that of Sky Blue 4GL dyeings is slightly increased, and in all three cases the fastness to washing is increased, by the treatment. Adding Cuprofix S to the urea-formaldehyde solution minimises bleeding at

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S at this stage and still further increases the fastness to washing. However, the compatibility of the Cuprofix S with the anti-crease solution depends on the catalyst employed, and a preliminary test is recommended. Some fastness grades to light of untreated and crease-resisted dyeings include-

		Untreated	Trea
Blue L		 7	7
Blue GL	***	 7	7
Sky Blue	4GL	 5-6	6

METOMEGA CHROME RED 2GLL- This chrome dye is specially recommended for mixture dyeings on all forms of wool material, particularly when applied by the Metomega single-bath method. Dyeings are yellower and considerably faster to light than those given by Metomega Chrome Red GM. Some fastness grades on wool of dyeings produced by the Metomega single-bath method include—

Light 7, milling 4, carbonising 5.

Solar Discharge Brown G— This direct dye is chiefly recommended for dischargeable dyeings, alone and in mixtures with other fast-to-light dyes, on cellulosic fibres. Crease-resist finishing slightly improves the fastness of dyeings to light, while rubberising has no ill-effects. Some fastness figures on cotton include— Light 5-6, washing at

40°c, (medium dyeing) 3, perspiration 3.
SULFONINE SCARLET GWL—This is a neutral-dyeing acid dye giving bright orange-reds of good fastness to light and very good fastness to wet treatments. Particular fields of application include knitting yarns and fabric, blankets and melange hats, while it is very useful for dyeing unions of wool and cellulosic fibres. It is of interest on silk, and may be direct-printed on wool, silk, and viscose rayon, using a special method in the last case. Some fastness grades on wool include-Light 5, washing at 60°c. 4, perspiration 4-5.

SULFONINE YELLOW CSR—This milling acid dye, which is applied from an acetic or phosphoric acid dyebath, gives bright, reddish yellows which are nonphoto-tropic. Dyeings withstand chlorination and have good fastness to wet treatments, while the dye is unaffected by metals in the dyebath and exhausts well under neutral conditions. Some fastness grades include-Light 4-5, washing 3-4, milling 3-4.

THIONAL COLOURS-A range of twenty-five sulphur dyes is illustrated on cotton cloth in this pattern card, including the notably bright Thional Brilliant Violet S and Red Violet R. Two sets of fastness figures are appended alongside each set of dyeings, referring to a direct dyeing and an aftertreated dyeing respectively. Aftertreatment with a mixture of CuSO₄ and dichromate is used in each case except with Thional Red Violet R, where CuSO₄ only is used, Thional Dark Blue V, where sodium perborate is used, and Thional Brilliant Violet S, which is not recommended for aftertreatment.

XYLENE FAST BORDEAUX P- This is an addition to the Xylene Fast P range, and like the other dyes in this group is characterised by its ability to produce level dyeings of good wet fastness from a weakly acid dyebath. It is recommended for use alone or in mixtures for bluish reds, wines, and maroons, particularly on yarn and piece material. It is unaffected by acid solutions of dichromates, and is of interest on silk and nylon, having good affinity and a high saturation value on the latter fibre. Some fastness grades on wool include— Light 5-6, washing (40° c.) 4-5, perspiration (alkaline) 4.

Reports on German Industry

Leo Sistig, Krefeld Piece Dye Vat

FD 927/50*

Seven fully dimensioned drawings made in 1938. C. O. C.

Maschinenfabrik Gerber-Wanslesen, Krefeld Hank and Piece Dyeing Machines FD 928/50*.

Fifteen fully dimensioned drawings made in 1935-1942.

Röhm & Haas G.m.b.H., Darmstadt Trade Pamphlets for Textile Auxiliary Agents

FD 681/50* (PB 81,071-81,082, forming part of PB 17,683).

Pamphlets, dated 1938–42, detailing in German the properties and application of the various brands of Silkovan, Eropal, Olgon, Immofil, Plexileim, Plexigum, Plextol, Acrisin, Degomma DL, and Paraffion double conc.

Deutsche Celluloid-Fabrik A.-G., Eilenburg Polyamide Solutions and Pastes

FD 833/50* (PB 31,536).

The mixed condensates from dibasic acids having > 3 C between their amino groups and ω -aminocarboxylic acids having > 4 C between their amino and carboxyl groups or their amide-forming derivatives, e.g. lactams, esters, and chlorides, quickly dissolve at room temperature in ethylene chlorohydrin. Such solutions when mixed with softening agents can be used as coatings for paper, textiles, artificial leather, wood, metals, etc. C.O.C. artificial leather, wood, metals, etc.

Henkel & Cie, Düsseldorf Progress Reports 1935-42

FDX 842* (PB 74,565; Microfilm J 279).

Reports in German covering work on production of melamine and dicyandiamide, methyl cellulose, carboxymethyl cellulose and other cellulose ethers, synthetic drying oils and detergents, farina and its derivatives, binders for paints, etc. The application of the products is also discussed. C.O.C.

I.G. Farbenindustrie A.-G., Hoechst Transketone (1:5-Dibenzoylnaphthalene)

FD 903/50* (PB 40,451).

Microfilm of a description, written in German in 1940, of the plant and method used for producing 1:5-dibenzoylnaphthalene from naphthalene and benzoyl chloride. was used as an intermediate for yellow Indanthren dyes. C. O. C.

I.G. Farbenindustrie A.-G., Leverkusen Progress Reports during 1929-44 on Preparation and Properties of New Compounds for Use as Dyes, Detergents, or Plasticisers

FDX 858* (PB 73,887; Microfilm N 65).

Numerous reports (800 pp.) in German, mostly written during 1940-44, dealing with aliphatic and aromatic compounds.

I.G. Farbenindustrie A.-G., Leverkusen Plastics, Dyes, Intermediates, and Textile Chemicals

Chemicals and Eulan NKA; and many organic products suitable for use in the rubber, plastics, and linoleum industries.

I.G. Farbenindustrie A.-G., Fechenheim, Frankfurt a. M. Organic Preparations, mainly Dyes and their Intermediates

FDX 866* (PB 74,236; Microfilm D 206).

Among a large number of manufacturing instructions are those for the following auxiliary products—

Ampho Soap 18 Cutisan 8

Soromin 8

Tallosan S

Wool Resist CB

Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Boad, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

and for the following dyes

Acid Leather Brown EMK and ER

Algol Yellow GGC Alphanol Brown R

Ambi Brown

Anthracene Acid Brown G; Chromate Brown BB [?EB]; Chrome Blue F, FR, G, N, and R; Chrome Brown SWN; Chrome Red G; Yellow C

Anthralan Orange GG, Violet 2R

Benzo Viscose Grey 5B Brilliant Congo R Celliton Fast Blue FFG

Chrome Fast Red B and G

Chrysophenine G (comparison of Leverkusen and Acna

processes) Columbia Green G

Cotton Brown A and N

Diamine Brown N; Chrome Brown G; Fast Red F; Golden Yellow; Green A, B, CL, FG, and G; Nitrazol Brown B, BD, G, and RD; Oral [sic] Brown G Diaminogen Blue G; Sky Blue N Diazo Fast Yellow 3GL

Helindon Chrome [sie] Green G Immedial Bronze RL; Catechu 1747 and F5RL; Khaki GRL; Leuco Olive B; Olive LB; Yellow Brown GCL and GL

Indanthren Blue Green FFB; Olive Green B, GB, and GG; Yellow 6GD and 6GD Suprafix

Indocarbon CLN

Isochrome Green 3BF Lanacyl Blue BB

Lanafuchsin 6B

Naphthamine Direct Black ANF

Oxydiamine Black JE

Sirius Supra Olive CL; Scarlet A, GG, and 3G

Sudan Brown 2RN; Red 2G; Yellow GR

Sulphur Dark Blue Tannin Orange R

Triazol Green Tropaeolin O.

C. O. C.

I.G. Farbenindustrie A.-G., Fechenheim, Frankfurt a. M. Progress Reports for 1931-45 on Organic

Preparations, mainly Dyes and Intermediates, Textile Chemicals, Solvents, and Plasticisers

FDX 861* (PB 74,237; Microfilm D 211). Numerous reports (1059 pp.) on work on dyes for wool, cotton, and acetate rayon, textile auxiliary and finishing agents, melamine, acrylic, and cyanamide resins, etc.

I.G. Farbenindustrie A.-G., Leverkusen Reports on Dyes, Intermediates, Auxiliary Agents, and Plastics

October 1940-April 1941 FDX 845* (PB 74,677; Microfilm L 88).

Microfilm of 130 laboratory reports (932 pp.) in German dealing with many types of dyes, 3:4-dichlorophenylsocyanate of 3'-amino-3:4-dichlorodiphenylsulphone-5-sulphonic acid (a very efficient mothproofing agent), detergents, Solidogens, animalising agents, polyurethan fibres, etc.

I.G. Farbenindustrie A.-G., Leverkusen Dyes and Intermediates—Eulans

FDX 850* (PB 74,919; Microfilm T 28).

Microfilm (749 pp.) of annual progress reports covering 1936–1939 from the various intermediates, dyes, and Eulan research sections. There are also four reports written in 1936, two of them dealing with the preparation of organic compounds, one with detergents and mercerising assistants, and another with the mothproofing of mixed fibres with Eulan NK, showing that thorough washing with Igepon T removed any of the Eulan NK from the vegetable fibres and so avoided the danger of reduction in light-fastness of the material. The manufacture of Brilliant Discharge Blue G, Celliton Fast Yellow 7G, and Chromoxan Brilliant Violet 5R is given. C. O. C.

I.G. Farbenindustrie A.-G., Leverkusen Progress Reports dated 1930-43 on Researches on Dyes and Intermediates, Textile Chemicals, and Mothproofing and Animalising Agents FDX 859* (PB 73,902; Microfilm N 62).

A large number of reports (811 pp.) dealing mainly with intermediates and dyes but including some on Solidogens; Eulans; animalising agents; cellulose esters, ethers, and disocyanates; Ultrasan and similar optical bleaching agents; plasticisers for cellulose acetate; etc. C. O. C.

I.G. Farbenindustrie A.-G., Leverkusen Progress Reports on Work during 1929-44 on Dyes and Intermediates, Textile Chemicals, Mothproofing Agents, Chlorinated Rubber, Plasticisers and Emulsifiers, Water-repellent Agents, Tanning Agents FDX 857* (PB 73,910; Microfilm N 57). Alerge number of percent (850 np.) in German, many on

A large number of reports (850 pp.) in German, many on dyes and rubber. Among the products dealt with are Acid Alizarin Blue Black R

Anthrasol Orange IGG

Hansa Red B

Indanthren Brilliant Blue R; Brilliant Green FFG; Brown NR; Khaki GR

Permanent Red R extra, and Katanol V and various Persistols.

I.G. Farbenindustrie A.-G., Ludwigshafen Working Instructions for Manufacture of Dyes 1932-45

FDX 872* (PB 82,025; Microfilm X 33).

Thirty-four sets of instructions for making various acid, basic, and fat-soluble dyes, the works (not the sales) names for which are given.

I.G. Farbenindustrie A.-G., Fechenheim

Frankfurt a. M.

Dyes and Intermediates, Textile Chemicals,
Finishing Agents, Resins, and Varnishes

FDX 863* (PB 82,189; Microfilm D 213).

Microfilm (820 pp.) of progress reports covering 1930–45. They deal mainly with the manufacture of dyes, but also with some auxiliary agents, e.g. Intrasol, Solidogen BS, and Thiazol BR. C. O. C.

I.G. Farbenindustrie A.-G., Frankfurt Dyes and Plastics FDX 855* (PB 74,234; Microfilm D 210).

Microfilm (1027 pp.) of methods of making Guinea Brown GRL, Rapidogen Golden Yellow IGL, and Supramine Brown GR; also of numerous annual progress reports on work on intermediates, dyes, and plastics covering 1930–1944. C. O. C.

I.G. Farbenindustrie A.-G., Bitterfeld Purification of Boiler Feed Water—Composition of Dyes and Proprietary Chemical Products Meetings of the I.G.'s Inorganic Research Committee (ANWIKO) FDX 860* (PB 73,962; Microfilm AA 155). Among a large number of miscellaneous laboratory and

Among a large number of miscellaneous laboratory and works reports dated 1929-44 are a number dealing with the treatment of boiler feed and cooling waters. There are a considerable number on auxiliary agents, including-Ampho Soap 18 and DN tech.

Etingal A new

Metachrome Mordant

Mollescal B

Protectols

Soligen Cobalt.

Reports on dyes deal with, amongst others-

Benzo Viscose Blue 3GFL

Celliton Red Brown 5R and other acetate rayon dyes Corial colours

Eukasol colours

Fanal Blue B

Fanal Bremen Blue G supra

Fast Coating White C

Palatine Fast Brown GN and other Palatine Fast dyes

Ursol Chrome dyes

Variamin Blue salt

Vulcan Yellow Zapon Fast Green 2G.

C. O. C.

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Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

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I.G. Farbenindustrie A.G., Agfa Kamera-Werke Munich

Dyes and Intermediates, Detergents, Textile Chemicals, Substitutes for Leather and Rubber, Bibliographies of Iron and Nickel Carbonyls

FDX 854* (PB 74,805; Microfilm O 225).

Reports on research work during 1939-43 on many intermediates and dyes, organic chemicals, plastics, sizing of paper pulp, nylon, Lumogens, detergents and auxiliary

I.G. Farbenindustrie A.-G. 1937 Intermediates (Zetko) Conference

LUDWIGSHAFEN WORKS

FD 677/50* (PB L 58,764-L 58,790, forming part of PB 14,998).

Microfilm copy of the following papers, among others, in German-

German—

(1) Present State of Work in the Vinyl Ether Field [Appretan WL and Plasticisers] (W. Reppe)

(2) Present State of Work on N-Vinyl Compounds [Luvicans] (W. Reppe)

(3) Water-soluble Intermediates—Addition of Maleic Acid to Primary N-Alkyl- and N-Hydroxyalkyl-amines [Textile Auxiliaries] (W. Reppe and H. Hiller)

Water-soluble Intermediates-- Addition of Maleic Acid and Fumaric Acid to Sulphinic Acids [Inter-

mediates for Acetate Rayon Dyes] (H. Ufer)
(5) Water-soluble Intermediates—Addition of Acrylic and Methacrylic Acids or their Esters and Nitriles to Sulphinic Acids [Dye Intermediates] (H. Ufer)

(6) Water-soluble Intermediates— Addition of Acrylic and Methacrylic Acids to Ammonia, Primary and Secondary Amines, and Ring NH Groups [Inter-

mediates for Dyes] (W. Reppe and H. Ufer) Vinyl and Ethyl Ethers of Aromatic Hydroxyalkyl-amines [Intermediates for Acetate Rayon Dyes (W. Reppe and H. Ufer)

(8) Reaction of Sulphinate Salts with Chloroacetic Acid,
 Ethylene Chlorohydrin, and Sodium β-Chloroethanesulphinate [Dye Intermediates] (H. Ufer)
 (9) Reaction of Urea Aluminium Chloride with N-Mono-

ethylaniline (H. Ufer)

(10) Addition of Nitromethane to Vinyl Ether, Sulphide, Sulphoxide, and Sulphone (W. Reppe and H. Ufer) (11) Addition of Aerylic Acid, Aerylonitrile, and Aerylate Esters to Phenolic Hydroxyl Groups [Dye Inter-mediates] (H. Ufer) (12) Coal Pressure Esterat (Characterists)

(12) Coal Pressure Extract [Cheap Leather Dye] (Schuster and Janson)

Glycide Compounds [Stabilisers for Compounds containing Chlorine] (Schuster and Aurnhammer) (13)

(14) Condensation Products from Crotonaldehyde [Textile Auxiliaries] (W. Schmidt and Thewalt)

(15) Action of Concentrated Alkali on o-Chlorophenol (a Contribution to the Knowledge of Multiple-ring Systems) (Schnell)

(16) Reactions with Alkyl and Hydroxyalkylamines

[Plasticisers and Developer BS (Ethyl-β-Naphthyl-amine and its Hydrochlorides)] (Holsten) Work concerning Leuna Alcohols [Nekal A and S, Dispersing Agent for Powdered Printing Dyes]

(18) Improvement in the Manufacture of Leonil S (Kaupp and Wappes)

(19) Investigation of F.P. 788,285 [Action of Oleum on p-Dichlorobenzene].

HOECHST WORKS

FD 656/50* (PB 58,703-58,731, forming part of PB 14,998). Microfilm of 37 papers in German, including the following-

(1) Reactions of Active Chlorine Compounds (a-Chloroalkyl Esters and a-Chloroalkyl Ethers) [Textile Chemicals, etc.] (Fitzky) (2) β-Pyridiniumbutyric Acid Betaine [Additive to Vat

Dye Printing Pastes] (Kracker and Fitzky)

(3) Work on Organic Chlorine and Fluorine Compounds [Increase of Light Fastness of Azoic Dyes by Trifluoromethyl Group] (Scherer et al.)

(4) Trifluoromethylanthraquinones (Scherer Schumacher)

itration of Trifluoromethylphenyl Sulphides (Schumacher and Müller) (5) Nitration

Dinitrobenzotrifluoride, Dinitrochlorobenzotrifluorides and their Reaction Products (Heyna)

Phthalic Acids containing Trifluoromethyl Groups (Kracker and Müller)

Monoarylides of Aromatic Dicarboxylic Acid Halides (Schumacher)

Naphtholsulphonyl Chloride and its Reactions [Azo Dyes containing the Sulphino Radical] (Sieglitz and Mahler)

(10)

and Manner)

Some 4-Substituted Salicylic Acids (Luce)

Rearrangements by means of Aluminium Chloride—

Dyes from 1:3-Dichloro-4-6-dinitrobenzene (Corell
and Popp)

Work in the Terpene Field [Depanol N IV, J IV,
and J] (Heisel and Dewein)

Derivatives of Outpropaline Bases (Jatz) (11)

(12)

(13)

Derivatives of Quinoxaline Bases (Jatz) Carboxyl Derivatives of Triarylcarbinols (Becker) (15) Production of Water Softeners by the Chloroacetic
 Acid Process [Trilon A] (Kissling and Schörnig)
 (16) Safe Method of Preparing Finely Divided Benzoyl
 Peroxide (Kracker and Jacobs).

WOLFEN WORKS

FD 679/50* (PB L 58,803-L 58,814, forming part of PB 14,998).

Microfilm of eleven papers in German, including the following—

(1) Production of Quinone and Quinol (Wesche et al.)

1:8-Dicyanonaphthalene (Rudolph) N:a-Divinyleneindole by Dehy

Dehydrogenation a-Benzylpyridine (Prager) Substantive Textile Auxiliaries [Solidogen WM,

Animalising Cellulose Fibres, etc.] (Brodersen and Quaedvlieg)

(5) Decacyclene and Dinaphthylenethiophen [Sulphur Dyes] (Rieche)

(6) Fur Dyes [Ursatins] (Lehmann).

LEVERKUSEN WORKS

FD 659/50* (PB L 58,744-L 58,763, forming part, of PB 14,998). Microfilm of nineteen papers in German, including the

(1) Chlorination of Diphenylene Oxidiphenylene Oxide] (F. Hommen) Diphenylene Oxide [3-Chloro-

Replacement of Chlorine by Hydrogen in Aromatic Chlorosulphonic Acids [3:5-Dinitrobenzene sulphonic Acid] (Nordt)

Quinol (Seydel)

4:6-Dichloro-2-aminodiphenyl Ether [Intermediate for Vat Pinks] (H. Hoyer)

(5) 3.4-Dicyanodiphenyl and Diphenyl-3:4-dicarboxylic Acid [Components for Copper 4:4':4":-Tetra-phenylphthalocyanine] (Rinke)

Diaminodiphenoxyacetic Acid and its Homologues
[Intermediates for Benzo Fast Copper Dyes]
(Taube and Delfs)

Copper Complexes of o-Phenylenediamine Deriva-tives as Agents for Aftertreating Substantive Dyes (Petersen)

New Intermediates from β -Naphthoic Acid (Tietze) Syntheses of 1:4:5:8-Derivatives of Naphthalene (9)

(Tietze) 4-Aminonaphtheultame as Bases for Naphtol AS (10)(Ballauf)

Hydroxycarboxylic Acids of Dihydronaphthopyrazine (Ballauf).

GRIESHEIM WORKS

FD 657/50* (PB 58,732-58,738, forming part of PB 14,998). Microfilm of the following six papers in German-

Substituted Alkoxy-p-benzoquinones Dimethoxyaminodiphenyl Sulphones (Ingelbert and (2) Hasenkamp)

Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

- (3) Nitroquinol Monoalkyl Ethers (Engelbert and Cissie)
- Halogenoand Nitrohalogeno-hydrocarbons by Displacing Nitro Groups in Polynitrobenzenes (Engelbert and Hasenkamp)
- (5) Chlorination of m-Nitrotoluene—Isomeric Chloro-nitrotoluenes and Attempts to Separate them (Engelbert and Weissbach)
- (6) Increasing the Yield when making 4:6-Dinitro-ocresol (Engelbert and Weissbach).

MAINEUR WORKS

- FD 658/50* (PB 58,739-58,743, forming part of PB 14,998). Microfilm of five papers
 - (1) Substituted o-Aminophenol Ethers [Intermediates for
 - Supranol Brilliant Reds] (E. Korten and Schultis)
 (2) 4-Aminopyrocatechol 1:2-Dialkyl Ethers (Riedmair)
 (3) Azo- and Azoxy-arylpolycarboxylic Acids (Schubert
 - and Honold) (4) Industrial Production of 4:4'-Dichloro-3:3'-dinitro-diphenyl Sulphone—Intermediate for Supranol Brown 3GL (Ritter)
 - (5) Nitro- and Amino-phthaloperinones (Brunner).

UERDINGEN WORKS

- FD 678/50* (PB L 58,791-58,802, forming part of PB 14,998).
- Microfilm of the following papers in German—
 (1) Catalytic Alkylation of Aromatic Amines and the Catalytic Splitting off of Ammonia by Metal Chlorides (Kasper)
- (2) Continuous Production of Ethylaniline (Adrian) (2 papers)
- Benzoylated Alkylanilines and Alkyltoluidines (Kasper)
- Catalytic Diphenylamine Process (Kasper)
- (5) Removing Poisonous Materials from the Waste Gases from Phosgenation with Simultaneous Utilisation of the Phosgene and Volatile Ester Components (Kasper)
- (6) Sulphoacetic Acid as Catalyst in Reactions of Unsaturated Hydrocarbons, especially in Production of Ethers of Secondary Alcohols (Kastner)
 (7) Condensation of Aldehydes with Cyanoacetic Acid
- and Analogous Compounds (Hamann)
 Unsaturated Ketones of High Molecular Weight (Buschmann)
- Salicylaldehyde and Coumarin (Müller)
 Reactions of Alkyl-substituted Aromatic Hydrocarbons (Binapfl and Pinkernelle). (10)

C. O. C.

I.G. Farbenindustrie A.-G. 1938 Intermediates (Zetko) Conference

WOLFEN WORKS

- FD 740/50* (PB L 58,924-L 58,938, forming part of PB 14,998).
- Microfilm of fourteen papers in German, including the following
 - (1) Phenyl Benzyl Sulphones [Intermediates for Black Dyes for Wool] (Wesche and Mathauser)
 - Tetrahydroquinolines from 1(or 2)-Methylepichlorohydrin [Intermediates for Acetate Rayon Dyes] (Lange)
 - (3) 1-Sulphomethyl-4-chloro-5-hydroxynaphthalene (Lange).

LUDWIGSHAFEN WORKS

- FD 712/50* (PB L 58,885-L 58,904, forming part of PB 14,998).
- Microfilm of nineteen papers in German, including the following-
 - (1) Some Derivatives of Dihydroresorcinol (Schuster et al.)
 - (2) N-Phenylpyrrolidine [G.P. Application I 60,947]
 - (Schuster et al.)
 (3) Condensates from Vinyl Methyl Ketone and Carbonyl Compounds [Dye Intermediates] (Hopf)

- (4) Indolenines and Indolines from Methyl isoPropyl Ketones [Intermediates for Acetate Rayon Dyes] (Kochendoerfer)
- (5) Derivatives of 1:8-Naphthylenediamine and of 1:8-
- Aminonaphthol (R. Schweizer)
 (6) p-Benzylaminophenol (T. Götz).

LEVERKUSEN WORKS

- FD 697/50* (PB L 58,870-L 58,884, forming part of PB 14,998).
- Microfilm of fourteen papers in German, including the
 - (1) Production and Use of Titanic Esters [Very Finely Divided Titanium Dioxide] (Nelles)
 Aromatic Amines containing Thiosulpho and Thio-
 - carboxyl Groups [Intermediates for Acetate Rayon Dyes] (H. Kleiner)
 - (3) Diphenyltricarboxytic Acids [Diphenyl-2:4:5-tri-carboxylic Acid, a Direct Cotton Dye] (Schröter,
 - Rinke, and Eck)
 (4) [Cheaper Methods of Preparing] 2:3-Dihydroxy-naphthalene, 2:3-Aminonaphthol, and 2:3-Diaminonaphthalene (Holtz)
 - (5) 2:5 and 2:8 Aminonaphtholdisulphonic Acids (Goll)
 - Degradation Products from Starch [Textile Finishes]
 (Nordt) (6)
 - (7) Ash-free Tanning Materials (Bauer).

HOECHST WORKS

- FD 689/50* (PB L 58,815-L 58,850, forming part of PB 14,998).
- Microfilm of forty-three papers, including the following-
 - (1) m-Chlorobenzotrichloride (Miller)
 - S·CF₃·Substituted Benzoyl Fluorides (Scherer) Reactions of Nitrophenyl Trifluoromethyl Sulphoxides
 - and Sulphones (Schumacher) Nitrotrifluorothioanisoles (Scherer)
 - Reduction of Nitrophenyl Trifluoromethyl Sul-phoxides (Schumacher)
- Trifluoromethyl-substituted Diphenyl Derivatives (Heyna)
- (7) Dinitration of Some Substituted Anilines [3:5. Dinitro-2-amino-4-methyl-1-anisole, 4-Chloro-3:5-dinitro-2-amino-1-anisole, and 3:5-Dinitro-2aminoquinol Dimethyl Ether-Intermediates for Azo Dyes] (Heyna)
- 2:3-Hydroxynaphthaldehyde (Luce)
- 4-Substituted 2-Hydroxy-3-naphthoic Acids (Kracker and Jacobs)
- (10) 3-Hydroxyquinoline-2- and -4-carboxylic Acids (Kracker)
- (11) Benzo-3-hydroxydiphenylene Oxide and Hydroxybenzoxanthen (Schimmelschmidt and Pfeuffer)
- 3-Hydroxycarbazoles (Zahn)
- (13) Reaction Products of NN'-Ethyleneurea and their Uses [Fatty Iminazolines as Plasticisers, Aftertreating Agents for Direct Cotton Dyes, and Textile Auxiliaries] (Bestian).

GRIESHEIM WORKS

DYE INTERMEDIATES -- ANTIOXIDANTS

- FD 690/50* (PB L 58,851-L 58,860, forming part of PB 14,998). Microfilm of nine papers in German
 - Aminated Benziminazoles (Wolf)
 - [Antioxidants from the Products of the Reaction of Methylamine with Nitrochlorobenzenes] (Wolf)
 - m-Chlorophenol [from m-Dichlorobenzene] (Weisbach) 2-Chloro-5:6-dinitrotoluene and its Reaction Pro-
 - ducts (Weisbach) Action of Nitric Acid on Quinol Acetate
- (B. Klarmann) Chloro-substituted Ethers of Polyphenols (B. Klarmann)
- Action of Aluminium Chloride on Nitroquinol Dimethyl Ether (B. Klarmann)
 - 3-Chloro-4-toluidine (Fiala and Scriba)
- Aminodiphenyl Sulphones (Hasenkamp and Fiala).
- Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

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MAINKUR WORKS

INTERMEDIATES FOR DYES AND RESINS

FD 691/50* (PB L 58,861-L 58,869, forming part of PB 14,998).

Microfilm of nine reports in German—
(1) Aminoaryl Sulphones from Halogenoaryl Sulphones

Higher Nuclear-alkylated Aromatic Amines (E. Korten)

(3) p · Hydroxyphenyl · β · naphthylamine (Korten and Loewe)

(4) [4-Chloro-3-nitrobenzonitrile (for making 2-Nitro-4-cyanodiphenylamine, a Greenish-yellow Acetate Rayon Dye of Excellent Light Fastness) from p-Chlorobenzaldehyde] (Ritter)

(5) Industrial Preparation of 4-Methoxynaphthostyril and its Intermediates 1:5-Hydroxynaphthoic Acid and 4-Hydroxynaphthostyril (Kunze)

(6) N - Substituted 4 - Hydroxynaphthostyrils, naphthostyril, and their Derivatives

(7) A Dibenzopenthiophen Sulphone [and its Effect on the Light Fastness of Fast Scarlet Base LG] (Schütz)

(8) Industrial Production Methods for Melamine (Keller)

(9) Constitution of Dehydrothiotoluidinesulphonic Acid (Schubert).

OPPAU WORKS

INTERMEDIATES FOR TEXTILE CHEMICALS—SOLVENTS

FD 713/50* (PB L 58,905-L 58,910, forming part of PB 14,998).

Microfilm of six papers in German-(1) Alkylated Formamides (Seid (Seidler) - Dimethylformamide is an excellent solvent for cellulose esters and ethers and many other organic compounds

(2) [Two Methods of] Preparing Adipic Acid [for Use in Linoleum Manufacture] (Speer and Weissbach)
 (3) Composition of the Oily and Aqueous Condensation

Products formed during the Oxidation of Paraffin Wax (Keunecke and Kürzinger)

(4) First Runnings Fatty Acids, Stearic Fatty Acids, and Distillation Residues in the Production of Soap Fatty Acids by Oxidising Paraffin Wax (Harder)

(5) Ketones and Secondary Alcohols from First Running Fatty Acids from Oxidation of Paraffin Wax (von Reibnitz)— Those from the C₇-C₉ fraction are particularly valuable as intermediates for wetting agents

(6) By-products in Production of Fatty Acids from Paraffin Hydrocarbons.

UERDINGEN WORKS

INTERMEDIATES FOR DYES AND AUXILIARY AGENTS FD 739/50* (PB L 58,911-L 58,923, forming part of PB 14,998).

Microfilm copy of twelve papers in German—
(1) Catalytic Production of Diphenylamine from Aniline (Krey)

Phenyl isoCyanate [from Diphenylurea] (Krey)

Acardite (Kasper)

(4) High-molecular Unsaturated Amides and Amines (Kastner)

Continuous Production of Ethyl Chloroformate (5)

(Kasper) Continuous Chlorination of Toluene (Pinkernelle)

Synthesis of a Mixture of o- and p-Oxylyl Chlorides (7)(Pinkernelle)

Substituted Benzyl and Menaphthyl [Naphthylmethyl] Chlorides (Pinkernelle)

Preparation and Use of Allylphenols (Bellefontaine and Buschmann)

Higher Alkylated Salicyclic Acids (Müller)

(11) Splitting of Dibenzyl Ether [quantitatively into Benzaldehyde and Toluene] (Binapfl and Pinker-[quantitatively into nelle)

(12) β-Substituted Acroleins (Coenen).

I.G. Farbenindustrie A.-G., Leverkusen Reports from the Azo Dyes Section during 1937-44

FDX 851* (PB 74,885; Microfilm T 25).

Some 150 progress reports in German, together totalling 795 pp., dealing with dyes, intermediates, plastics, and other organic products.

I.G. Farbenindustrie A.-G., Frankfurt a. M. Paints, Coatings, Protective Agents, etc. FD 838/50* (PB 65,976-66,078 and 86,941-86,943, forming

part of PB 19,932).

Microfilm of abstracts in German of 105 papers (285 pp.) read at the I.G.'s Building Materials Conference during 1934–42. Many of them deal with inorganic pignents, paints, and fireproofing preparations. Lead cyanamide, a lemon-yellow pigment, is three times as effective as red lead in rustproofing properties. C. O. C.

I.G. Farbenindustrie A.-G., Frankfurt a. M. X-Ray Examination of Polyamide Fibres FD 829/50* (PB 25,620).

Microfilm of three papers in German, written in 1938, 1939, and 1941 respectively-

(1) X-Ray Examination of Polyamide Fibres (20 pp.)
(2) X-Ray Examination of Stretched Polyamide Fibres

(18 pp.) Behaviour of Polyamides at High Temperatures
(28 pp.)
C. O. C. (25 pp.).

The Textile Printing Industry in Germany FD 848/50* (PB 27,730) [FIAT 558—unpublished]. A report (67 pp.) written by Allied investigators in 1946. The German printing industry had been slow to test new chemical processes developed by the I.G., and con-sequently the latter's most advanced ideas had first been put on a practical basis in other countries. Mechanical improvements, on the other hand, were quickly adopted. Dyeing machines were of excellent design, and most were covered to save steam and improve working conditions. Production in print works is extremely low, even taking into account the small runs handled by some plants. New aids to printing specially noticed were the Flu-Tex light, spiral doctor blades, vacuum strainers, and single roll mills in colour shops.

German Methods for Finishing Rayon Fabrics Textile Series, Report No. 21. FD 849/50* (PB 27,732)

Film strip of a report (73 pp.) written in 1946 by Allied nvestigators after visiting 15 German and Austrian works. The methods observed were similar to those in other countries, but some of the machines used for dyeing viscose rayon were remarkable for steam economy, ease of operation, and mechanical perfection. A process for producing combined water-repellency, crease-resistance, and low residual shrinkage in spun rayon fabrics was noteworthy in that a thick, suedy, full handle was first produced by chemical shrinkage, instead of trying to obtain the whole of the handle by a resin treatment.

Developments in the Wear Resistance of Textiles, and Related Papers published in Germany during World War II

FD 898/50* (PB 99,296).

A volume (368 pp.) of translations from articles appearing in Melliand Textilberichte during 1939-47 and from

unpublished papers. It is divided into five parts—

I—Evaluation of Serviceability and Wear Resistance

II—Chemical and Photochemical Degradation of Cellu-

III— Investigation and Classification of Fibre Properties IV— Fibre Structure and Reactivity of Fibres

V — Resistance to Water and Shrinkage, Laundering.

Röhm & Haas, Darmstadt Waterproofing and Sizing of Textiles and Paper Research Reports for 1936-45

FDX 827* (PB 74,527; Microfilm 288 I).

The first half of this microfilm consists of reports, written during 1932-46, on work on many aspects of the waterproofing and sizing of textiles, particularly with aqueous emulsions of paraffin wax. The second half

Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobalds Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

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consists of progress reports, dated 1936-45, mainly about work on the production and properties of methacrylate and methacrylamide resins and polymers. C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen Synthetic Resins and Varnishes Crêpe Finish on Silk FDX 837* (PB 82,027; Microfilm X 18). Among a number of reports, written in 1941–45, and

dealing with varnish and lacquer ingredients and manufacture, there is one describing a crêpe finish on silk obtained by the use of a Desmophen varnish. C. O. C.

Röhm & Haas, Darmstadt Methacrylate Polymers and Copolymers FDX 840* (PB 74,074; Microfilm C 283).

Numerous reports, written in 1937-49, on many aspects of the manufacture and application of methacrylate polymers and copolymers, including the use of Plexileim in textile finishes, Acrisins for finishing paper, fibres from methyl methacrylate—acrylonitrile copolymers, colouring of methacrylate polymers, etc. C. O. C. of methacrylate polymers, etc.

Röhm & Haas, Darmstadt Textile Finishing Agents—Tanning Agents FDX 824* (PB 74,552; Microfilm 291 I).

Routine reports from the research department during 1936-45 on work carried out on the use of the firm's products in textile bleaching, dyeing, finishing, and printing and in leather tanning.

I.G. Farbenindustrie A.-G., Frankfurt (Main)-Höchst
Textile Chemicals and Finishing Agents— Leather Greases

FDX 838* (PB 84,619; Microfilm O 44).

Numerous reports in German, dated 1938-44, on the manufacture and application of emulsifying and detergent agents, waterproofing agents, ethyleneimine and other "animalising" agents, formalising of cotton, etc., including few on leather greases.

C. O. C.

Röhm & Haas, Darmstadt .
Use of Cellulose Derivatives, Synthetic Resins, and Polymers in Coatings and Lacquers FDX 809* (PB 74,101; Microfilm C 279).

A large number of reports, written in 1938-45, including one on the effect of pigments on Plexigum-benzyl cellulose films and one on the behaviour of colouring matters in acrylic resin emulsions and coatings prepared from them. C. O. C.

Leather and Fur Processing

FDX 844* (PB 74,951; Microfilm W 15 [W 14]).

(1) Handbuch der Gerbereichemie und Lederfabrikation, Vol. 1, Part 1 (Dresden: W. Grassmann)— This portion of

the microfilm is a copy of pp. 707-1104 of the book, the first 700 pages of this part being on Microfilm W 14.

(2) Die Lederaustauschstoffe, by P. Fischer and F. Kemphe (Munich and Berlin: Lehmann 1942)—A book

of 180 pp.
(3) Chemie und Technik der Rauchwarenveredlung berufs Krankheiten, by R. Fritzsche (Leipzig: P. Schops 1940) Three alphabetical lists of works dealing with the processing of furs.

(4) Occurrence, Significance, and Nature of Relaxation Shrinkage in Human and Animal Hairs, by Lochte and Brauckhoff—Copy of an article which appeared in Der Rauchwarenmarkt (30, No. 11-16) dealing with the shrinkage of stretched hairs on being moistened.

(5) CHEMISCHE FABRIK STOCKHAUSEN & CIE., KREFELD Textile Auxiliary Agents and Agents for Processing Furs and Leather -- An undated list of 65 preparations for the textile and fur industries, giving full details of the application of each, is followed by a supplementary list dated Oct. 1943. There are copies of the patent applications made during 1935-44 on the processing of furs and skins. Two reports, written in 1938 and 1942 respectively, deal

with the manufacture and application of greases and oils for the fur and leather trades. There are three lists pre-pared in 1935, 1936, and 1937 of competitors' products for the leather industry, an analysis being given in each case. There is also an undated report on various agents for use in C. O. C. fur dressing.

[Mono- and] Polyvinylcarbazole in Germany FD 867/50* (PB 33,272).

Microfilm copy of an 11-pp. report by Allied investigators. It deals with the production of the monomer and the polymer (*Luvican*), which was used as a substitute for mica and asbestos. Tables give the properties of the polymer and of copolymers with styrene. C. O. C.

Plastics in Germany 1939-45

FD 831/50* (PB 28,316).

Microfilm of a report (78 pp.) issued by Allied investigators and giving a broad survey of the development of the German plastics industry.

I.G. Farbenindustrie A.-G.

Plastics and Lacquers FDX 811* (PB 82,015; Microfilm 19 X).

Reports, written in 1943–45, on the use of various resins, plasticisers, cellulose nitrate, etc. in the production of coatings and lacquers.

I.G. Farbenindustrie A.-G. Resins, Plasticisers, etc. for Impregnating Textiles and Paper and for Lacquers **Luminous Paints**

Lowering the Oil Absorption of Pigments Weathering of Kontrazit Colours FDX 812* (PB 82,032; Microfilm 14 X)

Reports, written in 1939—40, on various aspects of the manufacture of paints and lacquers, rubber finishes, treatment of pigments, oil substitutes for use in making leather cloth and oiled silk, impregnants for paper, Lumogen Yellow LG, etc.

I.G. Farbenindustrie A.-G., Ludwigshafen Plastics for Linoleum, Artificial Leather, and Adhesives

FDX 835* (PB 74,988; Microfilm X 26). A large number of reports, written in 1940. C. O. C.

A large number of reports, willows.

Manufacture of Laminates in Germany
FD 868/50* (PB 33,273).

Microfilm copy of a 20-pp. report written by Allied investigators on German methods of making paper- and C. O. C.

I.G. Farbenindustrie A.-G., Leverkusen Standard Methods of Analysis FD 696/50* (PB 67,548, 68,007, 69,127-69,612, 86,529-

86,537, forming part of PB 17,692; Microfilm C 113). A collection of 528 standard analytical methods used in the I.G. laboratories for both inorganic and organic C. O. C.

I.G. Farbenindustrie A.-G., Ludwigshafen Analytical Methods for Dyes, Intermediates, Auxiliary Agents, etc. FDX 867* (PB 74,979; Microfilm 61 X).

Microfilm of some 88 analytical methods for dyes, intermediates, auxiliary agents, etc., including a rapid method for estimating Soromin SG (hexaglycol monostearate) in the bath.

Siemens & Halske A.-G., Berlin-Siemensstadt Colouring of Metals

FDX 261* (PB 74,049; Microfilm B 262).

Amongst numerous reports written in 1933-46 are several dealing with Eloxal oxidised coatings on Al, including their colouring and the fastness to light and weathering of 16 dyes used; surface colouring of metals with chemicals; dyeable anodic chrome coatings on Zn; blue-black coating of Zn by use of 2% NaOH and D.C. (G.P. 606,502).

Material available for inspection at, and photocopies available from, T.I.D.U., Board of Trade, Lacon House, Theobaids Road, London W.C.1, or (under PB No.) from Office of Technical Services, Department of Commerce, Washington D.C., U.S.A.

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Abstracts from British and Foreign Journals and Patents

(The Titles of Patents are abridged and modified)

I-PLANT; MACHINERY; BUILDINGS

PATENTS

Rayon - spinning Machines. Courtaulds Ltd. and Industrial Rayon Corpn. B.P. 642,847.

A continuous rayon-spinning machine comprises two or more series of stepwise mounted thread-advancing reels, each series being driven by a single shaft and all these shafts being in turn driven by a horizontal main driving shaft. Connection of the driven shafts to the driving shaft is effected through clutches comprising a number of dises each provided with circumferential lugs on the former, and on the latter a cylindrical member provided with corresponding slots. The surface between the slots is chamfered to direct the lugs smoothly into place, thus enabling each series to be stopped individually without interrupting the rest of the frame.

J. W. B.

Cloth Guides. J. Dungler. B.P. 643,583.

Apparatus is described whose efficient operation is unaffected by variation in the width of the cloth being guided and which can be adjusted to avoid unnecessary actuation of the guiding when the selvedge is slightly irregular without sensibly affecting the accuracy of guiding. C. O. C.

Pressure Rollers. B. H. Wilsdon, A. J. P. Martin, and O. N. Thompson. B.P. 641,466.

The pressure about the line of contact of a pair of rollers is controlled by direct application of fluid pressure either directly to the external surfaces of the rollers or indirectly to their internal surfaces through the medium of hydraulic plungers. By this means load is applied uniformly to the rollers; thus there is no tendency for them to bow, and smaller and/or lighter rollers may be used than have hitherto been necessary to obtain the same pressure.

C. O. C.

Open-width Feeding of Fabrics of the Below-bathsurface Current Conveying Feed-slot Type. Fair
Lawn Finishing Co.

B.P. 641,172.

A convex surface has a vertical downwardly extending end portion. Treating liquor is passed continuously on to and over this surface toward and over the end portion. The fabric is brought in open, tensionless state on to this surface, and is carried by the flow of liquor into the bath. Even with delicate fabrics there is no undue grip on them, but nevertheless all crimps, etc. are removed from the fabric before it enters the bath.

C. O. C.

J-Boxes. C. T. Graham and Defiance Manufacturing Co. U.S.P. 2,503,817.

A J-box is described in which the cloth is accumulated and compacted in an ordered mass, so that when the leading end of the cloth reaches the discharge point the cloth can be drawn off promptly and effectively without snarling or tangling.

C. O. C.

Continuous Drying of, or Extraction of Moisture from, Cloths at Full Width. J. Dungler.
B.P. 641,963.

The open-width cloth is fed in absence of tension between the outer surface of a rotating perforated drum and the inner surface of an endless conveyor band that is permeable to gas and liquids. The surfaces of the drum and the band move at the same speeds. Dry unheated gas is fed under pressure to the interior of the drum. The machine is particularly suitable for drying or hydroextracting light and delicate fabrics.

C. O. C.

Stenters. Mather & Platt Ltd. and R. C. Mather.

B.P. 643,062.

An endless band, belt, or chain travels in the same direction and at the same speed as the clips, and makes such an angle to their line of travel that they are opened and closed gently without friction.

C. O. C.

Uniformly Drying and Curing a Resin-impregnated Endless Wool Felt, C. B. Albright and Orr Felt & Blanket Co. U.S.P. 2,512,128.

Screen Printing Stencil Frame. Severoceske Strojirny S.N.P. B.P. 641,996.

The side members of the frame consist of a profiled tube, which is resistant to bending and is formed with a single receas of dovetail form in which a strip of readily melted material is inserted. The gauze is embedded in the surface of this strip.

C. O. C.

Coating Paper, Cloth, etc. Virtu Inc. B.P. 642,902. A tank containing the coating material has a feed passage leading to an outlet mouth, a movable member with a surface in adjustably close proximity to the outlet and adapted to travel past it, and one or more smoothsurfaced feed rolls touching the coating material. Portions of the rolls form part of the wall of the feed passage, these rolls rotating so as to feed the coating material from the tank by frictional contact with them through the passage and the outlet mouth and against the adjustable surface under the hydraulic pressure thus generated mechanically. The outlet mouth can be adjusted to regulate its area and dammed to alter the thickness of coating delivered. The pressure at which the coating material is applied to the paper, etc. passing the outlet is regulated by varying the speed of the movable portion of the wall.

S. V. S.

Cloth Inspection Machine for Use where the Fabric is plaited after Inspection. F. S. A. Brett.
B.P. 643,406.

Garment-washing Machines. B. Morton and J. H. Perkins. B.P. 642,603.

The container for the material being washed has a spherical wall and a flexible diaphragm shaped to conform closely with the interior of the wall and fastened to it by a fluid-tight connection at the rim of the diaphragm. A separator has intercommunicating spaces to allow free flow of liquid between the diaphragm and the adjacent spherical wall. Means are provided for admitting liquid into these spaces. The cleansing liquor is squeezed from the material in the machine by introducing fluid pressure between the end walls of the container and the adjacent diaphragms so as to displace the latter.

C. O. C.

Laundry Washing Machine. C. J. Brennan.

A steam generator for periodically injecting steam into the wash liquor rests on the bottom of the washing chamber. It consists of a steam-accumulating chamber having an open end resting upon and closed by the bottom of the washing chamber. This chamber has an outlet member having its lower end within and well below the top of the chamber.

C. O. C.

Automatic Addition of Diluted Bleach to Washing Machines. C. R. W. Smart, W. E. Pugh, and Baker Perkins Ltd. B.P. 643,116.

Laundry Washing Machine automatically controlled throughout a Complete Cycle of Operations. G. C. Graham, D. B. Graham, G. H. Barker, and Graham & Barker. B.P. 643,486.

Rotary Garment Presses. J. Simpson and J. Simpson, Jr. B.P. 643,270.

A device is described for leading live steam to, and removing exhaust steam from, stationary to moving parts without loss of steam or risk of burns to the operator.

Garment Press. J. Simpson and J. Simpson, Jr. B.P. 643,285.

A vertically movable ram is placed beneath a fixed press head. A horizontally rotatable carrier has two tables which can be brought in turn between the ram and the head. The carrier is rotated mechanically by simple but reliable means in which complex control arrangements and reliance upon spring action are avoided. C. O. C.

Steaming Valves for Garment Presses. Prosperity Co. Inc. B.P. 642,978.

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Automatic Forming Machine for Felt Hats. M. Cassó. B.P. 643,137.

The perforated former is mounted on a movable vertical support in such a way that it can pivot a quarter of a revolution about a horizontal axis at right-angles to its axis of revolution. This enables the former to be in a vertical position for spraying, thus facilitating subsequent downward removal of the hood.

C. O. C.

Coating Paper. C. P. Putnam, W. E. B. Baker, and New York & Pennsylvania Co. Inc. U.S.P. 2,511,415.

Applying Transfers to Earthenware, Johnson Brothers (Hanley) Ltd. and G. W. Bird. B.P. 642,548.

II— WATER AND EFFLUENTS

Developments in the Treatment of Dye House Wastes. S. I. Zack. Sewage Wks. Engng., 20, 129, 130, 172, 173 (1949): Water Pollution Abs., 23, 20 (Jan. 1950).

An account of the system in use at a Dallas Pa. works, where suspended solids and B.O.D. (biological oxygen demand) are reduced from 207 to 18 p.p.m. and from 697 to 53 p.p.m. respectively.

C.O.C.

Further Experiments with Synthetic Detergents at Huddersfield, particularly with respect to their Action on Percolating Beds. H. H. Goldthorpe and J. Nixon. J. R. Sanit. Inst., 70, 116-130 (1950): Water Pollution Abs., 23, 13 (Jan. 1950).

Experiments showing that, with Lissapol N (ICI) or Teepol X (Shell) in sewage, percolating filters may remain unaffected for months, but that in the course of time they become badly choked compared with filters treating sewage not containing detergents of those types. C. O. C.

PATENTS

Boiler Composition. Geigy Co. Ltd., G. A. Campbell, and H. Lomas.

B.P. 642,238.

The tendency of finely divided solids present in boiler water to form scale is removed by adding to the water being heated in a preheater or economiser a sodium salt of a naphthalenesulphonic acid-formaldehyde condensate known to be a dispersing agent for pigments. C. O. C.

Removing Dissolved, Suspended, or Colloidal Matter from Liquids. Infileo Inc. B.P. 641,964.

Apparatus is described in which the raw liquid is treated with a coagulant and/or precipitant in a circulating slurry comprising suspended particles separated and accumulated from previously treated liquid. C. O. C.

accumulated from previously treated liquid. C. O. C.

Removing Suspended Matter from Effluents containing Colloidal Protein Material. W. Seifriz, E. J. McCue, and E. S. Mead. U.S.P. 2,511,299.

The effluent is brought to pH 9–10·8 by adding alkalimetal or alkaline-earth compounds, and then 0·5–2 grains of $\rm ZnCl_2$ or $\rm ZnSO_4$ per gal. (U.S.A.) of effluent is added as a coagulant. C. O. C.

Regeneration of Ion Exchangers. Dorr Co.

The regenerant chemical remaining in the exchange bed towards the end of regeneration is collected in a sequence of different concentrations by passing wash water through the bed and collecting the first portion of the effluent which has a concentration of unspent regenerant nearly as high as that of the regenerant solution. Then a portion of effluent in which the regenerant is considerably diluted with wash water is collected, and enough regenerant added to it to bring the concentration above that of the first portion of the effluent. The first less concentrated and the second highly concentrated solutions are then used, one after the other, for regenerating a bed of exchange material.

III— CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Preparation of Sodium Carboxymethyl Cellulose. S. M. Brown and G. H. Thomson. J.S.C.I., 69, 254 (Aug. 1950).

A readily soluble sodium carboxymethyl cellulose is prepared by grinding together alkali cellulose and sodium monochloroacetate and maintaining the mixture under pressure for 24 hr. The required amount of monochloroacetate is incorporated in four stages with intermediate compression.

W. K. R.

Mechanism of the Action of Copper 8-Quinolinoxide. R. E. Vicklund and M. Manowitz. CADO, Tech. Data Digest, 15, (5), 18-21 (1950): Chem. Abs., 44, 7476 (25th Aug. 1950).

Cu 8-quinolinoxide dissociates to form 8-hydroxyquinoline (I) and Cu ions, each of which performs different but uniquely related functions. I inhibits growth of fungi by precipitating metals which are essential for their growth. Fungi are capable of destroying the activity of I, probably by oxidation. The Cu ions interfere with the metabolic process or product which destroys I; thus both the Cu ions and I are necessary to achieve maximum fungistatic activity.

C. O. C.

PATENTS

Stabilisers for Soap. Monsanto Chemical Co. and G. D. Martin. B.P. 642,596.

Incorporation of a little of an alkali-metal or ammonium thiocyanate, mercury thiocyanate, an alkyl, aralkyl, or alkylene thiocyanate, guanidine thiocyanate, or an aryl mustard oil stabilises soap against change in colour and odour.

C. O. C.

Soapless Detergents containing Acid Triphosphates as Builders. Procter & Gamble Co. and O. T. Quimby. B.P. 642,921.

Any water-soluble acid triphosphate of general average formula $M_xH_{5-x}P_sO_{10}$ (M = an alkali metal, x=3-5) has a building action superior to the normal completely neutralised salt when mixed with an anionic detergent. C. O. C.

Glassy Phosphate Powder Compositions. Albright & Wilson Ltd. and C. J. Munter. B.P. 642,944.

The individual particles of the phosphate glass are coated with an acid reversion product of the glass and then mixed with a substance which reacts with the acid reversion product to release a gas when placed in water. The product does not tend to cohere and rapidly dissolves without stirring when added to water.

The particles of phosphate glass are coated with an acid or a substance which reacts with acid to release a gas, and then mixed with a material which reacts in water with the acid coating to produce a gas or an acid which reacts with the coating to release a gas.

C. O. C.

Cellulose Sulphate. J. C. Thomas and Du Pont.
U.S.P. 2,511,229.

Cellulose sulphates having < 0.5 combined SO₄ for each glucose unit are obtained by impregnating cotton linters with an equal weight of a solution of 20% by weight of sulphamic acid, 40% of urea, and 40% of water, drying the linters, and then heating at 135-140°c. for 30 min. The products are useful as textile sizes and finishes and for preparing fibres and films.

C.O.C.

Aqueous Dispersion of Glycol Phthalate-Adipate-Starch Substitute. O. C. Bacon and Du Pont. U.S.P. 2,511,895.

The condensate of 5-15 mol. of adipic acid, 95-85 mol. of phthalic anhydride, and enough ethylene glycol to esterify all the COOH groups can be obtained in stable aqueous dispersion by first mixing it with aqueous ammonia at 75-95°c. in a heavy-duty mixer. Incompletely saponified polyvinyl acetate (saponification number 127-200, viscosity of 4% aqueous solution at 20°c. measured by a Hoeppler viscometer 40-50 centipoises) is dissolved in water at 75°c, and added to the ammonia-resin mixture with viscous milling to form a water-in-oil emulsion. This is then cooled to 50-55°c., after which water and acetic acid are slowly added to invert the suspension. The product is used as a substitute for starch in sizes and finishes for textiles. Addition of a cationic dispersing agent to the final dispersion renders it substantive to textile fibres, enabling them to be treated by a process in which the bath is exhausted as distinguished from the straight padding used in absence of the cationic dispersing

Surface-active Materials. Sharples Chemicals Inc. B.P. 643,456.

Polyethylene glycol thioethers, useful for wetting and washing fibrous materials, are prepared by condensing ethylene oxide with a tertiary alkyl thiol derived from a polymerised olefin and containing (a) 8-24 C atoms, the stoichiometric ethylene oxide: thiol ratio being 2-28:1;

(b) 10-14 C atoms, with a ratio of 4-16:1; or (c) 12-16 C atoms, with a ratio of 4-20: 1. In one example ethylene oxide (3285) reacts with a mixture of 95% tert.-dodecyl thiol (2480) and sodium methoxide (117), the stoichiometric ratio of 6.41: 1 giving the maximum efficiency in the final product. J. W. B.

Wool - wax Alcohol Products. Fulmer Research Institute Ltd. and E. S. Lower. B.P. 643,422. Surface-active properties and/or solubility of mixed wool-wax alcohols are improved by reaction at 130-170°c. with addition of contabilities in the surface of the surface with ethylene oxide, with addition of a catalytically active base such as sodium methoxide. In one example mixed wool-wax alcohols (100) and sodium methoxide (1), dissolved in the minimum amount of methanol, react under a pressure of 1.3-3.5 atm. and at 130-170°c. with sufficient ethylene oxide to give an approximate ethylene oxide: starting material molecular ratio of 5:1. The product is a useful emulsifier for oil-in-water emulsions.

J. W. B. Polyethylene Glycol Ethers of Bis(tetra - alkyl-hydroxyphenyl)methanes — Surface - active Agents. L. H. Bock, J. L. Rainey, and Röhm & Haas Co.

U.S.P. 2,504,064.

Compounds of formula-

$$\begin{array}{c|c} \mathbf{H} \cdot [\mathbf{O} \cdot \mathbf{R}^1]_s \cdot \mathbf{O} & \mathbf{O} \cdot [\mathbf{R}^1 \cdot \mathbf{O}]_s \cdot \mathbf{H} \\ & \mathbf{R}^3 & \mathbf{CH}_g & \mathbf{R}^3 \\ & \mathbf{R}^4 & \mathbf{R}^2 & \mathbf{R}^4 \end{array}$$

(R¹ = alkylene of 2-3 C; R² and R³ = hydrocarbon groups each of 1-18 C; R⁴ and R⁵ = H or hydrocarbon groups each of 1-18 C; the sum of the C atoms in R², R³, R⁴, and R⁵ = 5-20; x = 4-20) are non-ionic, surfaceactive substances which are unusually efficient emulsifying agents under a wide variety of conditions. C. O. C.

Acylpolyalkylene-polyamine and Auxiliary Agents, General Aniline & Film Corpn. and F. J. Gajewski.

B.P. 642,989. and Auxiliary Agents.
Corpn. and F. J. Gajewski.
Compounds of formula—

 $R^{1}\cdot CO\cdot NH\cdot [CHR^{2}\cdot CHR^{3}\cdot NH]_{x}\cdot C(:NH)\cdot NH\cdot C(:NH)\cdot Y$ $(R^1 = \text{sat. or unsat. aliphatic hydrocarbon radical which may be substituted by hydroxy groups; <math>R^3$ and $R^3 = H$ or CH_3 ; x = 2-4; $Y = NH_2$ or $NH_2 \cdot R^4 \cdot X$ ($R^4 = C_{1-5}$ Alk; $X = \text{Hal or } O \cdot SO_3 \cdot R^3$; $R^5 = C_{1-5} \cdot Alk$) are produced by heating an acylpolyalkylene-polyamine with dicyandiamide. They are used as dye-fixing agents on cellulosic fibres, softening agents, etc. C. O. C.

Tri- and Tetra-substituted Biguanides. American B.P. 643,012. Cyanamid Co.

Compounds of formula-

R1-NH-C(:NR3)-NH-C(:NH)-NR3-R4

or their acid addition salts (R^1 and R^2 = aromatic, aliphatic, alicyclic, araliphatic, or heterocyclic radicals (excluding the case when R^1 = halogenophenyl and R^2 = Alk); R^2 and R^4 = H, aromatic, aliphatic, alicyclic, aralkyl, or heterocyclic radicals, but only one of them may be H, or may jointly form a heterocyclic ring with the N atom to which they are attached (but excluding the case in which R1 and R2 are both alkyl, R3 is aromatic, and R4 is H or Alk)) are useful as textile and dyeing assistants, vulcanisation accelerators, etc. C. O. C. vulcanisation accelerators, etc.

NN'N''-Triacylmelamines. W. S. Emerson, T. M. Patrick, and Monsanto Chemical Co. U.S.P. 2,507,700.

Compounds of formula-

(R = Alk of 4-17 C) are waxy, crystalline products, of m.p. 130-230°c., insoluble in water and organic solvents and very resistant to hydrolytic agents. They may be used in the production of water-repellent finishes on

Pesticidal Compositions. B. F. Goodrich Co.

B.P. 642,534. Compounds of general formula R 1.S.NR 2 (R 1.S : residue obtained by removing the H atom from the SH group of a thiol compound; NR 2 = residue obtained by removing an H atom from a primary or secondary amine), e.g. the sulphenamide of diethyldithiocarbamic acid and diethylamine, have excellent bactericidal, fungicidal, and insecticidal properties.

Ethyl Cellulose Hot-melt Coatings. Hercules Powder Co., G. H. Pyle, and J. S. Tinsley. B.P. 643,064. The lower alkyl esters of oxalic acid containing < 6 C in each alkyl group are colour stabilisers for ethyl cellulose hot-melt coatings. C. O. C.

Stabilising Thermoplastic Cellulose Ether Com-positions. Hercules Powder Co., W. W. Koch, and A. L. Rummelsburg. B.P. 643,348. p-cycloHexylphenol and SO_3 or a compound which when heated gives off SO_3 make an excellent colour stabiliser for cellulose ether compositions. C. O. C.

Imparting a Wrinkle Texture to Non-wrinkling Materials. W. F. Flanagan and New Wrinkle Inc. U.S.P. 2,510,966, U.S.P. 2,510,967.

Spraying water on to a non-wrinkling coating of a thermoplastic resin and a solvent, which is preferably warm, develops a uniformly patterned wrinkle finish. Suitable apparatus is described. C. O. C.

Blown Oils particularly suitable as Substitutes for Chamois Moellon in preparing Fat-liquoring Agents. Nopco Chemical Co. (XII, p. 664.)

IV— RAW MATERIALS; INTERMEDIATES; **COLOURING MATTERS**

Solvent Extraction of Tar Acids from Coal Tar Hydrocarbons. C. F. Prutton, T. J. Walsh, and A. M. Desai. Ind. Eng. Chem., 42, 1210-1217 (June 1950)

The solubilities of typical tar acids (phenol, p-cresol, β -naphthol, and p-tert-butylphenol) and hydrocarbons (methylnaphthalene, hexadecane, and 2:2:4-trimethylpentane) in mixed water-methanol solvents are given at 10°, 25°, and 35°c. A. S. F.

Separation of m- and p-Cresols by Liquid-Liquid Extraction. C. A. Walker. Ind. Eng. Chem., 42, 1226-1230 (June 1950). The appreciable difference in the ionisation constants of m- and p-cresol is the basis for a commercial method of separating them, capable of continuous operation. It involves distribution of the cresols between aqueous caustic soda and an organic solvent, such as benzene. A. S. F.

Sulphonation of Carbazole in Organic Solvents. V. F. Borodkin. J. Appl. Chem. (U.S.S.R.), 23, 759-762 (July 1950).

Isolation of Carbazole and Anthracene from Crude Anthracene. Idem. Ibid., 763-766.

The sulphonation of carbazole in soln, by chlorosulphonic acid leads to the formation of the 3-sulphonic acid and the 3:6-disulphonic acid, the ratio of the products depending on the amount of chlorosulphonic acid used, but not to an appreciable degree on the temperature and the duration of the reaction. When the reaction is carried out in presence N-sulphonic acid, but at higher temperatures the 3-sulphonic acid is formed. By treating crude anthracene with chlorosulphonic acid at 18-20°c. in presence of dimethylaniline, using chlorobenzene as diluent, the carbazole present may be converted into the N-sulphonic acid, the remaining constituents being unaffected. The N-sulphonic acid is separated as an aqueous soln., and is then hydrolysed with acid to regenerate the carbazole. The process is best carried out on crude anthracene which has been somewhat enriched by treatment with boiling water. The quality of the technical carbazole obtained is in no way inferior to that produced by methods involving treatment with pyridine bases or fusion with caustic potash.

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456. and sing m a the : 1; Kinetics and Mechanism of Aromatic Nitration-II-V. J.C.S., 2400-2473 (Sept. 1950).

Nitration by the Nitronium Ion, NO₂⁺, derived from Nitric Acid. E. D. Hughes, C. K. Ingold, and R. I. Reed. *Ibid.*, 2400–2440.

The kinetics of aromatic nitration are dealt with in the following sections

(1) Kinetic Orders of Aromatic Nitration: the Nitronium Aromatic nitration displays second-order kinetics in sulphuric acid, first-order kinetics in nitric acid, and zeroth-order kinetics in either nitromethane or acetic acid with nitric acid in constant excess for sufficiently reactive aromatic compounds, and first-order for sufficiently unreactive compounds. The data indicate that the kinetically fundamental process is localised in nitric acid, is activated, is heterolytic, and produces electron-deficient nitrogen by bond fission-

$$HO-NO_3 \rightarrow HO^- + NO_3^+$$

(2) Solute Effects on Nitration Kinetics: Mechanism of Formation of the Nitronium Ion— The data show that one proton is employed, and one nitrate ion eliminated, in the conversion of nitric acid into a nitronium ion. following two-stage mechanism is unequivocally established-

$$2HNO_3 \rightleftharpoons H_2NO_3^+ + NO_3^-$$
 (fast)
 $H_2NO_3^+ \rightarrow NO_2^+ + H_2O$ (slow)

(3) Medium Effects on Nitration Kinetics: Mode of Action of the Nitronium Ion-It is concluded that the nitrating attack must be a two-stage bimolecular process

$$ArH + NO_2^+ \rightarrow Ar^+H(NO_2)$$
 (slow)
 $Ar^+H(NO_2) \rightarrow ArNO_2 + H^+$ (fast)

The recently discussed suggestion that the nitrating attack is a one-stage termolecular process, requiring the collabora-tion of a base, and especially of an anion, as in—

$$NO_2^+ + ArH + HSO_4^- \rightarrow ArNO_2 + H_2SO_4$$

is disproved.

(4) Effects of Nitrous Acid on Nitration Kinetics: Contion of Nitrous Acid in Nitric Acid Solvents— Deprodition of tonation by the nitrite ion leads to retardation of nitration by a three-halves-power law. Nitrous acid exists in nitric acid mostly as N2O4, but an increase of concentration, or the addition of water, increases the small proportion in which it exists as N2O3. н. н. н.

 Nitration in Acidified Aqueous Nitric Acid.
 E. S. Halberstadt, E. D. Hughes, and C. K. Ingold. Ibid., 2441-2452.

IV—Nitration by Dinitrogen Pentoxide in Aprotic Solvents. V. Gold, E. D. Hughes, C. K. Ingold, and G. H. Williams. Ibid., 2452-2466.

- Nitration by Acyl Nitrates, particularly by Benzoyl Nitrate. V. Gold, E. D. Hughes, and C. K. Benzoyl Nitrate. V. Gold Ingold. Ibid., 2467-2473.

Directional Dependence of the Ultra-violet Absorp-tion of the Carbonyl Chromophore— I. J. O.

Fixl and E. Schauenstein. Sitzungsber. Öster. Akad.

Wiss., 159, (5), 598-605 (1950). The directional variations of the intensity of the ultraviolet absorption band for p-benzoquinone and the magnitude of the extinction coefficients are recorded and dis-It is found that the CO chromophore produces

appreciably greater absorption when its long axis falls in the plane of vibration of the light than when they are at н. н. н. an angle.

Study of Diazo-compounds by Use of Nitrogen Isotopes. I—Structure of the Diazonium Ion. P. F. Holt and B. I. Bullock. J.C.S., 2310-2311 (Sept. 1950).

The non-equivalence of, and absence of interchange between, the nitrogen atoms of a diazonium ion have been demonstrated by preparing the diazonium salt from demonstrated by preparing the discontinuous of the labelled and unlabelled sodium nitrite, coupling it with \$\textit{\beta}\$-naphthol, and regenerating the aniline by reduction of the azo compound. The analyses indicate that the reactions proceed according to the scheme-

$$\begin{array}{c} C_0H_5^{-15}NH_2 \xrightarrow{NaNO_2 + HCl} & [C_0H_5^{-15}N:N]^+\\ & & & \\$$

and that the diazonium is attached to the phenyl group throughout the synthesis.

Ultra - violet Spectrum and Constitution 3-Hydroxy-2-naphthoic Acid and Related Com-pounds. E. D. Bergmann, Y. Hirshberg, and S. Pinchas. J.C.S., 2351-2356 (Sept. 1950).

3-Hydroxy-2-naphthoic acid (I) and its methyl ester are yellow, whereas 1-hydroxy-2- and 2-hydroxy-1naphthoic acid and also 3-methoxy-2-naphthoic acid (II) and its methyl ester are colourless. To explain this surprising phenomenon, the ultra-violet (and visible) absorption spectra of I and its methyl ester have been recorded and found to be identical, whereas there are visible differences between the 3-hydroxy compounds and II and its ester: especially, the maximum at 3700 A. in the spectrum of the hydroxy acid is shifted into the ultraviolet (3400 A.) upon methylation. It is suggested that this difference is due to hydrogen bonding in the hydroxyl compounds, a viewpoint supported by infra-red spectra. The ultra-violet spectra of the O-methyl derivatives of the above, of salicylic acid and its ester, and also of certain acetylnaphthols are recorded. H. H. H.

Some Theoretical Considerations in Azo-pigment Chemistry. J. Glassman. J. Assocn., 33, 191-220 (May 1950). J. Oil & Col. Chem.

Modern theories relating colour and constitution are used to account for the hues of pigments. Acetoacetarylamides, because of their open chain structure, give yellow and orange pigments, while 2:3-hydroxynaphthoic arylamide coupling components produce the deeper red, violet, or blue hues owing to the highly conjugated naphthalene nucleus. The varying depths of shade of the nitroaniline- β -naphthol pigments are correlated with the position of the nitro group in the molecule. The light fastness of a pigment depends on the medium in which it is used, but certain groups in definite positions with respect to the azo group tend to give high light fastness. I.G. information on the use of aminodiaryl sulphones, trifluoromethylanilines, and halogenoaminoanthraquinones as diazo components is reviewed. The paper also takes into account conditions for coupling, the phenomena exhibited when an aqueous pigment paste is dried, and the effect of isolation conditions on such physical characteristics as brightness, strength, and intensity.

noazo Compounds from N-Arylglycamines. T. Matsukawa and K. Shirakawa. J. Pharm. Soc. Monoazo Japan, 63, 456-461 (1943): Chem. Abs., 44, 7329 (25th Aug. 1950).

Diazobenzene couples with some N-carbohydrate derivatives of 3:4-dimethylaniline to give azo compounds; e.g. 3:4-dimethyl-D-ribitylaminobenzene gives 2-D-ribitylamino - 4:5 - dimethylazobenzene, whereas with e.g. 4-methyl-p-arabitylaminobenzene a diazoamino compound

Azo Compounds prepared from Diazobenzene-arsonic Acids and Pyrroles. N. Muić and D. Flés. Arhiv Kem., 20, 92–96 (1948) [English summary]: Chem. Abs., 44, 6413 (25th July 1950). Diazotised arsanilic acid couples with 5-hydroxy-2-

methyl-3-carbethoxypyrrole to give a yellow dye. Diazotisation of 3-nitroarsanilic acid causes replacement of the nitro group by hydroxyl; this hydroxydiazo compound then couples with the above pyrrole derivative to give a Bis-p-aminophenylarsinic acid when diazotised and coupled with the same pyrrole derivative gives 4 - (5 - hydroxy - 2 - methyl - 3 - carbethoxy - 4 - pyrryl azophenyl)(p-aminophenyl)arsinic acid, a yellow azo compound, soluble in excess NaOH with a red colour. E. S.

Reactions with o-Amino- (and o-Nitro-)benzaldehyde — Ethylidene Homologues of Quinaldine, Azo Compounds, Azomethines. W. Borsche and F. Sell. Chem. Ber., 83, 78–87 (1950): Chem. Abs., 44, 5327 (25th June 1950).

Derivatives of quinaldine are formed by treating o-aminobenzaldehyde or its 4-methylanil with e.g. CH₃·CO·CH:CH·CH₃, which gives 2-propenylquinoline. In methyl alcoholic NaOH, compounds such as anhydrotris-o-aminobenzylidene-p-toluidine-

are formed. Such amino compounds can be diazotised and coupled with e.g. resorcinol to give azo compounds. Nitrobenzylideneanilines and related compounds exhibit

phototropy; e.g. N-o'-nitrobenzylidene-p-anisidine, prepared from o-nitrobenzaldehyde and p-anisidine, consists of bright yellow leaflets, which on irradiation turn black without change of m.p. and revert to yellow in the dark.

Colour and Constitution. I—Basic Dyes. M. J. S. Dewar. J.C.S., 2329-2334 (Sept. 1950).

The calculation of light absorption by the molecular-orbital method is discussed. While the process suffers from a number of major theoretical shortcomings (cf. Coulson and Dewar, Faraday Soc. Discussions, 2, 54 (1947)), it appears satisfactory for calculating the groundstate energies and electron distributions in hydrocarbons, and reasons are submitted to indicate that basic dyes and reasons are submitted to indicate that basic dyes should provide a favourable case for its application. This conjecture has been confirmed by agreement between the calculated and experimental absorption frequencies for— $(CH_3)_2N^+\cdot CH\cdot [CH:CH]_n\cdot N(CH_3)_4$ (n=1-3), Michler's hydrol blue, Malachite Green, Bindschedler's Green, Crystal Violet, Acridine Orange, 2:7-diaminophenazinium salts, sodio derivative of acetylacetone, sodium derivative of dibutterpreserving that

of dihydroresorcinol, and

NaO·[CH:CH]₃·CH:N·[CH:CH]₃·CHO

In consequence, a general molecular-orbital theory of such dyes has been proposed, which leads to a comprehensive set of rules for the effect of structural changes on light Н. Н. Н. absorption.

Components of Trifolium pratense L. I—Trifolin and Trifolitin. T. Nakaoki. J. Pharm. Soc. Japan, 63, 444-448 (1943): Chem. Abs., 44, 7315 (25th Aug. 1950).

Trifolitin and trifolin (cf. Power and Salway, Chem. Abs., 4, 1610) have been identified as having.

tetrahydroxyflavone 3-rhamnoside respectively.

C. O. C. 4, 1610) have been identified as kaempferol and 3:4':5:7-

C. O. C. Natural Anthocyanins. XVIII—Isolation of Natural Anthocyanins in the Blue Form and Determination of the Metallic Elements Present.

3. An Attempted Explanation of Variation in Colour of Flowers. XIX—Synthesis of the Blue Form of Anthocyanins and Comparison of it with the Naturally Occurring Form.

4. An Attempted Explanation of Variation in the Colour of Flowers. K. Shibata and K. Hayashi. Acta Phytochim. (Japan), 15, 219-222 and 223-227 (1949). Chem. Abs., 44, 7386 (25th Aug. 1950).

Colouring Matter of Gleditschia triacanthos. A. M.

Colouring Matter of Gleditschia triacanthos. A. M. Gakhokidze. J. Appl. Chem. (U.S.S.R.), 23, 747-749 (July 1950).

In previous work on the colouring matter of Gleditschia triacanthos two dyes were isolated. The structure of one of these, akrammerin, was determined, and it was synthesised (cf. J.S.D.C., 65, 184 (April 1949)). The other, a red substance, is now identified as 5:7-dihydroxy-4'-methoxyisoflavone and is given the name of olmelin.

A. E. S. Xanthopterin from Skins of the Yellow Mutant of Bombyx mori. Y. Hirata, K. Nakanishi, and H. Kilkawa. Science, 111, 608-609 (1950): Chem. Abs.,

44, 6977 (10th Aug. 1950).

The pigment in the skins of the yellow mutant of the silkworm has been identified as xanthopterin. C. O. C.

PATENTS

Multiple-step Process for Preparing NN'-Diphenyl-p-phenylenediamine. M. L. Clemens, J. E. Magoffin, and Eastman Kodak Co. U.S.P. 2,503,712.

Preparation of NN'-diphenyl-p-phenylenediamine from quinol and excess aniline proceeds in two stages—(i) condensation of aniline with quinol to form N-phenyl-p-aminophenol and (ii) condensation of the latter with aniline. The optimum conditions for the two steps are not the same, so that if attempts are made to carry out both reactions simultaneously the maximum yield cannot be obtained. C. O. C.

NN'-Diphenyl-p-phenylenediamine. H. G. Stone and Eastman Kodak Co. U.S.P. 2,503,778.

Trialkyl phosphates are very suitable catalysts for the reaction between aniline and quinol. They do not readily promote formation of tars or other undesirable by-C. O. C. products.

1-Cyanophenyl-3-acylamino-5-pyrazolone Colour Couplers. A. Weissberger, P. W. Vittum, C. O. Edens, and Eastman Kodak Co. U.S.P. 2,511,231. Compounds of formula-

$$\begin{array}{c} R^1 \\ | \\ N \\ OC \\ N \\ | \\ \parallel \\ H_2C \longrightarrow C \longrightarrow NH \cdot R^2 \end{array}$$

(R1 = mononuclear cyanoaryl, R2 = a carboxylic acyl radical) produce magenta images with primary aromatic C. O. C. amino developers.

Diacridyldiamine Derivatives. E. C. Britton, G. H. Coleman, and Dow Chemical Co. U.S.P. 2,503,899. The yellowish solids of formula-

(R¹ = lower alkoxy; R² = CH₂ or p-C₆H₄; Z = CH₂. CH(OH), or O; m and n = 0-2) are useful intermediates for dyes, while some have bactericidal properties. They are obtained by causing a compound of formula-

to react with one of formula NH₂·R ²·Z·R ²·NH₂. C. O. C.

Violet, Chromiferous Monoazo Dye. Ciba Ltd. B.P. 642,425.

A violet wool dye is made by treating the monoaco compound 2 - aminophenol - 4 : 6 - disulphonic acid $\rightarrow \beta$ -naphthol with chromium sulphate, which gives more p-haphthol with chromain supplies, which gives have level dyeings than the similar compound produced by acting on the same monoazo compound with chromium fluoride as described in B.P. 310,011 (cf. J.S.D.C., 46, 385 (1930)).

Metallisable Monoazo Dyes. J. R. Geigy A.-G.

Metallisable dyes, particularly suitable for chromeprinting on cotton, are made by diazotising compounds of formula-

(Y = SO₃H, arylsulphonyl of the benzene series, or alkylsulphonyl of < 5 C) and coupling in acid medium with-

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yl om. $(R=H,\,Alk,\,or\,Ar;\,\,Z=H\,\,or\,\,SO_3H).$ Thus 4-chloro-3-nitrobenzenesulphonyl chloride is condensed with 5-amino-3-methyl-2-hydroxybenzoic acid, and the Cl atom replaced by SO_2H by treatment with sodium sulphite. The NO_2 group is then reduced to NH_3 . The amino compound so produced is diazotised and coupled with 2-amino-8-naphthol-6-sulphonic acid under weakly acid conditions. The product, chrome-printed on cotton, gives bluish reds, and also dyes wool bluish red hardly changed on after-chroming. E. S.

Azoic Pigments from 5-Chloro-2:4-dialkoxyanilines.
W. H. von Glahn and General Aniline & Film Corpn.
B.P. 642,329.

Pigments are made by coupling diazotised 5-chloro-2:4-dialkoxyanilines (where the alkoxy is methoxy or ethoxy) with acetoacetic arylamides, arylamides of 2:3-hydroxynaphthoic acid, etc. Thus 5-chloro-2:4dimethoxyaniline diacetoacet-o-tolidide is a yellow pigment. E. S.

Brown Pigments for Viscose Spinning Solutions, etc. J. Glassman and I.C.I. Ltd. B.P. 642,204.

Chocolate-brown pigments are produced by coupling tetrazo compounds derived from benzidine and substituted benzidines with arylmethylpyrazolones in presence of highly dispersed carbon black. The methods used and the results achieved resemble those described in B.P. 604,875 (cf. J.s.D.c., 64, 410 (1948)), whereby monoazo pigments are generated in presence of carbon black. Mixtures of diamines diazotised and coupled with 1-p-tolyl-3-methyl-5-pyrazolone as in B.P. 621,599 and 633,215 (cf. J.s.D.c., 65, 493 (Oct. 1949); 66, 299 (May 1950)) are specially suitable. Thus, all parts being by weight, a mixture of 3:3'-dichlorobenzidine sulphate (245-7) and o-dianisidine (73-2) is tetrazotised, mixed with dispersed carbon black (200), and coupled with 1-p-tolyl-3-methyl-5-pyrazolone (376) in presence of caustic soda. The brown pigment, after filtering off and ball-milling with disodium dinaphthylmethanedi-\$\frac{\partial}{\partial}\text{sulphonate}, can be added to viscose spinning solutions for the production of deep brown fibres.

Acylaminoazo Dyes, and Dis- and Polyazo Dyes derived therefrom. Sandoz Ltd. B.P. 643,046.

derived therefrom. Sandoz Ltd. B.P. 643,046. Monoazo compounds derived from 2:8-aminonaphthol-3:6-sulphonic acid (\gamma\) acid), 2:8-aminonaphthol-3:6-disulphonic acid (\gamma\) acid), 1:5-aminonaphthol-7-sulphonic acid (M acid), and their N-alkyl and N-aryl derivatives, by coupling with diazo compounds in acid media, are themselves not capable of further coupling, but their N-acyl derivatives couple readily with diazo compounds. Thus the monoazo compound o-nitroaniline \(\frac{\lambda\cdot}{\rm \text{cd}} \rightarrow \gamma\) acid is acetylated with acetic anhydride in strong sulphuric acid, and the O-acetyl group hydrolysed by stirring in 10% aqueous caustic soda, to give the N-acetylaminoazo compound, which is capable of coupling with diazo compounds.

B.P. 643,054.

The N-acetylaminoazo compounds described in B.P. 643,046 above can be coupled with diazo compounds to give dis- and polyazo dyes. Depending on the intermediates selected the products dye animal or vegetable fibres or leather, or may be capable of giving metallic complexes. Thus the N-acetyl derivative of the monoazo compound 4-nitroaniline-2-sulphonic acid Acid y acid is coupled under alkaline conditions with 1-diazonaphthalene to give a brown-violet wool dye. By saponifying the N-acetyl group, a brown wool dye is produced. E.S.

Copperable Polyazo Dyes. J. R. Geigy A.-G.

B.R. 639,866.

Modification of B.P. 579,063 and 633,166 (J.S.D.C., 63, 122 (1947); 66, 300 (May 1950)). Tetrazotised 4:4'-diamino-3:3'-dialkoxydiphenyl compounds whose alkoxy groups may be substituted are coupled in any desired order with (i) 1 mol. of a dye of formula—

(R¹ = an aliphatic, aromatic, araliphatic, or alicyclic radical not bound through a CO group to the N atom; the benzene nucleus A may contain further substituents); and (ii) 1 mol. of an OH-containing coupling component which yields metallisable azo dyes or 1 mol. of a dye of general formula—

(R² = H, or an aliphatic, aromatic, araliphatic, or alicyclic radical not bound through a CO group to the N atom; B = the radical of any desired diazo compound, e.g. an o-carboxyphenyl radical). The products are dyes for cellulose, and can be aftercoppered to yield in some cases dyeings which are faster to light and/or water than those of the dyes described in the parent specifications.

C. O. C.

1-Amino-2-alkoxy-4-hydroxyanthraquinones — Dyes
for Cellulose Esters. Ciba Ltd. B.P. 641,561.

Pink dyes for cellulose acetate are made by treating a
1-amino-2-halogeno-4-hydroxyanthraquinone with a <
3% alcoholic solution of potassium hydroxide at > 100°c.

Thus 1-amino-2-bromo-4-hydroxyanthraquinone is converted to the 2-methoxy derivative by heating in an autoclave at 140°c. for 12 hr. with 1·25% methyl alcoholic potash.

R. K. F.

4 - Acylamino - 1 : 8 - naphthalimides — Fluorescent Lacquer Dyes. M. O. Shrader and General Aniline & Film Corpn. B.P. 641,569.

Blue-fluorescing dyes soluble in organic solvents and hence useful for colouring lacquers are made by condensing a 4-nitronaphthalic anhydride with ammonia or an amine, reducing the NO₂, and acylating the resulting amino derivative. Thus the compound—

is prepared by treating 4-nitronaphthalic anhydride with n-butylamine in boiling acetic acid. Iron powder is then added at $100^{\circ}\mathrm{c}$. over 1-2 hr. followed by acetic anhydride and further refluxing till acetylation is complete.

R. K. F.

Alkylcyclohexylaminoanthraquinones— Acid Dyes.
Sandoz Ltd.

B.P. 640,931.

Sandoz Ltd.

Blue acid dyes are prepared by condensing a 1-amino-4halogenoanthraquinone-2-sulphonic acid with a di- or
tri-alkylcyclohexylamine. Alternatively, the corresponding
2:4-dihalogenoanthraquinone may be used and the
2-halogen ultimately replaced by SO₃H by treating with
a sulphite. Thus the dye—

is made by heating sodium 1-amino-4-bromoanthraquinone-2-sulphonate with 1-amino-2:4-dimethylcyclohexane in water in presence of NaOH and Cu powder at 65°c. for 8 hr. R. K. F. elic the ts);

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 $\begin{array}{cccc} \textbf{Thiophanthraquinone} & \textbf{Derivatives.} & \textbf{H. R. Lee, V.} \\ \textbf{Weinmayr, and Du} & \textbf{Pont.} & \textbf{U.S.P. 2,501,131.} \\ \textbf{Mononitro derivatives of thiophanthraquinone} & & & & & & & \\ \end{array}$

are prepared by cyclising nitro-2-(2'-thienoyl)benzoic acids. Thus 6-nitro-2-(2'-thienoyl)benzoic acid is heated in 95% sulphuric acid at 145-150°c. for 2 min., and diluted in water to give 8-nitrothiophanthraquinone.

 $U.S.P.\ 2,501,132.$ The nitrothiophanthraquinones of $U.S.P.\ 2,501,131$ are reduced with e.g. ferrous hydroxide or alkaline sodium hydrosulphite to give the corresponding amino compounds.

Conditioning Anthraquinone Vat Dyes. Lewis Berger & Sons Ltd. B.P. 643,291.

Anthraquinone vat dyes are produced in pigment form by mixing them with aniline or a nuclear-substituted aniline and then separating the mixture into its components, e.g. by removing the aniline with a solvent. The treated dyes have one or all of the pigment propertieshigh tinctorial strength, improved mass tone, clarity of hue, and softness of particle. C. O. C.

Acridone-Carbazole Vat Dyes. F. Max, D. I. Randall, and General Aniline & Film Corpn.

U.S.P. 2,501,645.

Olive vat dyes are made by condensing anthraquinone 2:1-(N)-1':2'-(N)-4 benzoylamino -6' chlorobenz accidence with a 1-aminoanthraquinone containing in the 4- and/or 5-position(s) benzoylamino group(s) and cyclising the resulting product. Thus the dye-

is prepared by heating together at 210°c. for 4 hr. naphtha lene, 1-aminoanthraquinone, soda ash, copper acetate, and anthraquinone - $2:1 \cdot (N) \cdot 1':2'(N) \cdot 4$ - benzoylamino - 6'-chlorobenzacridone. The resulting anthrimide is separated by adding chlorobenzene and then cyclised by heating at 85°c, for 1 hr. in nitrobenzene containing aluminium chloride. R. K. F.

Copper Phthalocyanines. Sherwin-Williams Co. B.P. 640,576.

Copper phthalocyanine pigments are prepared by heating 4 mol. proportions of phthalonitrile with at least 1 atomic equiv. of copper in the form of the reaction product of ammonia and cupric acetate, in nitrobenzene saturated with ammonia, between 100°c. and the reflux temperature.

Cyanine Dyes containing a Sulphohydrocarbon Radical. R. H. Sprague and Eastman Kodak Co. U.S.P. 2,503,776.

Cyanine dyes having a sulphohydrocarbon radical in one or both of the auxochromophoric N atoms differ widely in properties from the corresponding known dyes containing carboxyalkyl groups. Dyes containing a sulphoalkyl group in only one of the auxochromophoric N atoms are zwitterions, whereas the corresponding carboxyalkyl dyes contain a separate anion. Replacement of carboxyalkyl radicals attached to both N atoms by sulphoalkyl radicals confers solubility in ethyl alcohol containing triethylamine.

Pyrrolocyanine Dyes containing a Carboxyalkyl or Sulphoalkyl Group. R. H. Sprague and Eastman Kodak Co. U.S.P. 2,503,775.

Dyes of general formula-

$$X\{R^1-N=(CH-CH)_n=C-CH=CH-C-CH$$

and

 $(R^1 = carboxyalkyl, R^2 = Alk \text{ or } Ar, n = 0 \text{ or } l, X = an$ anion, D = a bivalent hydrocarbon radical, Z = nonmetallic atoms necessary to complete a 5- or 6-membered heterocyclic ring) are readily soluble in mildly alkaline media. They are prepared by condensation of appropriate pyrrole-aldehydes and cycloammonium quaternary salts. C. O. C.

Pyrrocoline Polymethincyanine Dyes. R. H. Sprague, L. G. S. Brooker, and Eastman Kodak Co. U.S.P. 2,511,222.

Dyes of formula-

$$\mathbf{X}\{\mathbf{Alk}-\overset{\cdot}{\mathbf{N}}=(\mathbf{L}-\mathbf{L})_{n}=\overset{\cdot}{\mathbf{C}}-[\mathbf{CH}=\mathbf{CH}]_{d}-\overset{\cdot}{\overset{\cdot}{\mathbf{N}}}=\overset{\mathbf{Q}}{\overset{\cdot}{\mathbf{N}}}$$

(L = a subst. or unsubst. methin group; n = 0 or 1; d = 1 or 2; Z = non-metallic atoms necessary to complete a 5- or 6-membered heterocyclic nucleus; R1 and R2 H, Alk, or Ar; X = an anion; Q = atoms necessary to complete a pyridine nucleus) have powerful helminthicidal properties.

Polymethin Dyes containing a Triazole Nucleus. L. G. S. Brooker, R. H. Sprague, and Eastman Kodak U.S.P. 2,503,709.

Dyes of formula-

$$X\{R^1-N=(CH-CH)_n=C-CH=CH-C$$

(R¹ = alkyl, alkoxy, aralkyl, or carboxyalkyl; R² = subst. or unsubst. aryl; n=0 or 1; X = an anion; Z = atoms necessary to complete a 5- or 6-membered heterocyclic nucleus) are obtained by condensing a 4-formyl-2aryl-2:1:3-triazole with a cycloammonium quaternary salt containing a reactive methyl group. C. O. C.

Dyes for Antihalation Filter Layers. Gevaert Photo-Producten N.V. B.P. 642,728.

Dye salts of formula-

$$A \cdot R^1 \cdot CZ \cdot R^2 \cdot B^+ X^- \longleftrightarrow A \cdot R^1 \cdot CZ \cdot R^2 \cdot B^+ X^-$$

(A and B = auxochromes; R^1 and R^2 = benzene residues; X^- = an organic acid radical; and Z = H, residues; — an organic acturation, and the con-CN, or subst. or unsubst. CO.NH, or COOH) give anti-halation filter layers of extraordinary density, do not stain the fingers even when the wet emulsion is touched, and have good mechanical fastness.

Methin and Polymethin Dyes. H. D. Edwards and Ilford Ltd. Dyes of formula-

$$\vdots \dots \dots D \dots \dots \vdots \\ \mathbf{R^2-\dot{N}-(CH=CH)_n-\dot{C}=CR^1-CAlk=C(CN)-COOAlk} \\$$

 $(R^1 = H \text{ or Alk, } R^2 = Alk \text{ or aralkyl, } D = \text{residue of a}$ 5- or 6-membered heterocyclic compound, n = 0 or 1) are obtained by treating a compound of formula-

R3-S-CAlk:C(CN)-COOAlk

obtained.

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(R³ = Alk or aralkyl) with an alkyl or aralkyl quaternary salt of a 5- or 6-membered heterocyclic N compound having a reactive CH₂R¹ α or γ to the quaternary N atom.

B.P. 642,516. Methin dyes are obtained by treating a compound of formula R³.8-C(CH₂R¹):C(CN)-COOAlk with an alkyl or aralkyl quaternary salt of a 5- or 6-membered heterocyclic compound containing a thioether group α or γ to the quaternary N atom.

B.P. 642,517.

Polymethin dyes are produced by treating a compound of formula $R^3 \cdot S \cdot C(CH_2R^1) \cdot C(CN) \cdot COOAlk$ with a compound of formula—

$$X{R^2-N=(CH-CH)_n=C-CH=CH-Q}$$

(Q = S·Alk or an amino or subst. amino group; X = an acid radical).

Fractionation of Plant Pigments. R. Miller and Chemical Foundation Inc. U.S.P. 2,511,824. A method of separating the chlorophyll from the carotene in the concentrate obtained by extraction with paraffin hydrocarbons depends upon treating the concen-

paraffin hydrocarbons depends upon treating the concentrate with propane at 160°F. under sufficient pressure to keep the propane liquid. This yields two immiscible liquid phases, one containing more chlorophyll and the other more carotene than the concentrate. These fractions are again treated with liquid propane, and the operation is repeated until pure extracts of the two pigments are obtained.

γ-Ferric Oxide Hydrate and γ-Ferric Oxide. Columbian Carbon Co. and J. Martin.

C. O. C. Particle Columbian Carbon Co. and J. Martin.

B.P. 643,303.

The ferrous ion is precipitated from a solution of ferrous chloride by adding a solution of an alkali or alkaline-earth metal hydroxide at $150-200^{\circ}\mathrm{F}$. That temperature is maintained until the slurry is thin, and the latter is then diluted, cooled, and finally oxidised until the product is a clean orange-yellow. It gives the X-ray diffraction pattern of γ -ferric oxide hydrate. Heating it to $450-500^{\circ}\mathrm{F}$, dehydrates it and turns it brown, when it gives the ferric oxide X-ray diffraction pattern. C. O. C.

γ-Ferric Oxide Hydrate in Stoving Finishes. Columbian Carbon Co., C. D. Downs, and J. Martin.

B.P. 643,308. γ -Ferric oxide hydrate is particularly suitable for use in stoving finishes, the orange–yellow pigment on being heated in presence of oils or resins at $>300^\circ\mathrm{F}$. yielding a uniform brown. Its use results in tougher and more resistant films than does that of a-ferric oxide hydrates.

Titanium Pigments. National Titanium Pigments Ltd., J. T. Richmond, G. G. Durrant, and R. J. Wigginton. B.P. 642,979.

Rutile titanium dioxide is obtained by mixing a nucleated titanium salt solution (prepared by one of two methods described) with a hot aqueous medium at not < 70°c. to produce a concentration of Ti in the mixture (calc. as TiO₂) of 40–150 g./litre, heating to complete hydrolysis, and finally calcining the hydrous TiO₂ so obtained.

Rutile Titanium Oxide. C. M. Olson, J. E. Booge, and Du Pont. U.S.P. 2,511,218.

When the nucleating agent used for hydrolysing a titanium salt solution is prepared by treating hydrous TiO₂ controlled with respect to both basicity and acidity, it yields a hydrolysis precipitate (especially anatase) which, when calcined at a low temperature, such as that normally used in making anatase pigment, yields a high-quality rutile pigment.

C. O. C.

Heating Titanium Tetrachloride prior to mixing it with an Oxidising Gas to produce Titanium Dioxide. I. J. Krchma and Du Pont.

U.S.P. 2,512,341.

Titanium Oxide Pigments. A. J. Werner and Du Pont.
U.S.P. 2,512,079.

The chlorine adsorbed on titanium oxide produced by the oxidation of titanium tetrachloride vapour is removed by adding 0.5-10% by weight of an oxygen compound of boron to the pigment, heating at $500-750^{\circ}\mathrm{C}$, and separating the boron-containing titanium dioxide from the resulting non-adhering chlorine-containing products. C. O. C.

Chemical Constitution versus Printing Performance and Other Properties of Vat Dyes. L. D. Barrick. (IX, p. 661.)

Diazotype Material. General Aniline & Film Corpn., S. C. Slifkin, and H. C. Unkauf. (IX, p. 661.)

V-PAINTS; ENAMELS; INKS

Tint Retention of Coloured Paints based on White Pigments, C. T. Morley-Smith. J. Oil & Col. Chem. Assocn., 33, 249-269 (June 1950).

The comparative resistance to fading of coloured paints based on various white pigments has been studied. It was shown that zinc oxide and lithopone give much superior tint retention to antimony oxide, rutile and anatase titanium dioxide, and white lead. A. S. F.

PATENTS

Printers' Inks and Paints. H. G. Hoffmeister, A. H. Soane, and Usher-Walker Ltd. B.P. 642,797.

A smoky flame is directed on to a travelling solid surface bearing a film of oil or other liquid vehicle. The liquid is then collected, and if it does not contain enough carbon black it is passed again or repeatedly as a film to be subjected to the flame until the desired pigmentation is

Red-fluorescent Colouring Material. J. A. C. Yule and Eastman Kodak Co. U.S.P. 2,503,790. A mixture of equal weights of Xylene Red B (Colour Index 748) and Quinoline Yellow (C.I. 801) in an aqueous

Index 748) and Quincline Yellow (C.I. 801) in an aqueous borax solution of shellac has a fluorescence of the same hue and greater brightness than one with the same concentration of Xylene Red B alone. Addition of lithopone to the mixture improves the brightness of the fluorescence when the ink is used on a more or less transparent material. C. O. C.

Flatting Agent. A. Saunders and Interchemical Corpn. U.S.P. 2,512,470.

The Mg, Zn, Al, or alkaline-earth metal soaps of Manilla gum are excellent flatting agents for use in lacquers and synthetic resin coating compositions. They have good non-crazing properties and good solvent resistance.

Titanated Organosiloxy Compounds. H. C. Gulledge and Du Pont. U.S.P. 2,512,058.

The products obtained by interaction of an anhydrous liquid mixture of an ester of titanic acid and the hydrolysate of an organohalogenosilane of formula $R_n \mathrm{SiHal}_{b-n}$ (R = hydrocarbon radical of < 20 C, n=1-3) are filmforming compounds of good gloss and high durability. They form a paint vehicle of great transparency and excellent colour suitable as a varnish, useful in making white stoving enamels, and particularly well suited for incorporation therein of TiO_2 owing to its ease of dispersion in the titanated silicone vehicle.

C. O. C.

Emulsion Paints. Lewis Berger & Sons Ltd., D. H. Hewitt, and L. A. Paxon. B.P. 642,652.

A paint, which gives a glossy waterproof film, is readily thinnable with water, and can be applied to porous surfaces, is produced by dispersing with the aid of an emulsifying agent an air-drying oil vehicle in an aqueous dispersion of a pigment and a naturally occurring organic protective colloid. The weight of pigment is 0.25-2.0 times that of the air-drying vehicle. The weight of protective colloid is 8-20% of that of the air-drying vehicle and also 5-15% of the combined weight of pigment and air-drying vehicle. C. O. C.

Water Paste Paint. B. O. Newman and National Gypsum Co. U.S.P. 2,511,782.
Addition of organic tetra- and penta-hydroxy mono-

Addition of organic tetra- and penta-hydroxy monobasic acids or their water-soluble salts to water-thinned paste paints inhibits colour variation or flashing. C. O. C. Coating Compositions of Powdered Metal dispersed

Coating Compositions of Powdered Metal dispersed in Sodium Silicate. Industrial Metal Protectives Inc.
 B.P. 643,512.

 Powdered Zn, Pb, Al, Mg, Cd, and alloys thereof are

Powdered Zn, Pb, Al, Mg, Cd, and alloys thereof are dispersed in an alkali silicate solution in which the molratio of alkali oxide to SiO₂ is $1:2\cdot3-3\cdot0$. The metal pigment has an average particle size of 3μ , and at least 90% by weight must be capable of passing through a 400-mesh Tyler sieve. The products are not affected by moisture during stoving and do not give an efflorescence on the film when it is exposed to air.

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Pencil Leads. cil Leads. Koh-i-Noor Pencil Factory L. & C. Hardtmuth National Corpn. and V. Hrubas.

B.P. 642,619. Leads giving more intense impressions are obtained by making them from graphite or lampblack, clay, and salts of rare earth metals, e.g. Ce, Nd, Pd, Th, and La, of transition metals, e.g. Fe, Zn, or Co, or of alkaline-earth metals, e.g. Ba, which are not capable of vitrification, but which during the fusing of the leads gradually produce oxides which witrific to class that absorbs light.

C. O. C. which vitrify to glass that absorbs light. C. O. C.

Stabilising Thermoplastic Cellulose Ether Com-positions. Hercules Powder Co., W. W. Koch, and A. L. Rummelsburg. (III, p. 651.)

γ-Ferric Oxide Hydrate in Stoving Finishes. Columbian Carbon Co., C. D. Downs, and J. Martin. (IV, p. 656.)

Printing on Polyvinyl Resins. L. W. E. Townsend and Associated Technical Manufacturers Ltd. (IX, p. 661.)

VI —FIBRES; YARNS; FABRICS

Review of Research and Development in the Field of Textiles during 1949. Textile Research Institute and Textile Foundation. Text. Research J., 20, 612 (Sept. 1950).

Correction to previous paper, Text. Research. J., 20, 317–360 (May 1950): J.S.D.C., 66, 494 (Sept. 1950).

Dissolution of Cellulose in Organic Solvents. K. H. Meyer, M. Studer, and A. J. A. van der Wyk. Sitzungsber. Öster. Akad. Wiss., 159, (1-2), 151-154

Differences of solubility of crystalline and amorphous celluloses prepared from Lintra cellulose (a Swedish sulphite pulp suitable for rayon manufacture), in pyridine-chloral as solvent, are found to be due to the influence of crystallinity and molecular weight. The following additional solubility data are supplied for amorphous celluloses prepared from Lintra-cellulose and cotton respectively— The former are soluble and the latter insoluble in pyridine mixed with chloral, resorcinol, quinol, or pyrogallol, while both are soluble in quinolineresorcinol; also, the former are soluble in quinoline containing chloral, quinol, or pyrogallol, whereas the latter are only partly soluble. No solutions were obtained with pyridine or quinoline mixed with gallic, pieric, or pieramic acid, phenylhydrazine, urea, thiourea, guanidine, or formamide. The mechanism of dissolution is ascribed to either compound or addition-compound formation, whereby solubility in pyridine is brought about, and experiments in illustration of this viewpoint are described. It is also found that amorphous cellulose from Lintra fibre dissolves to form highly viscous stable solutions in pyridine—LiX, quinoline—LiX (X = Cl, Br, I), and pyridine—Ca(CNS)₂, whereas amorphous cellulose from cotton dissolves only in pyridine—LiBr and quinoline—Ca(CNS)₂. In no case does unprecipitated native cellulose dissolve. The specific character of the effect of electrolytes indicates that a purely electrostatic theory is insufficient to explain the phenomena. н. н. н.

Reaction of Cellulose with Alkalis. G. Petitpas. Mém.

Services chim. État (Paris), 34, 125–137 (1948): Chem. Abs., 44, 7534 (25th Aug. 1950). Swelling of cellulose in alkali of various concentrations proceeds in three stages—Up to 12% NaOH concn. there is penetration of water and NaOH into the amorphous areas. From 12 to 20%, NaOH is introduced into the crystalline areas with little added water being absorbed. Above 20%, both NaOH and water are again adsorbed. These three stages are also defined by X-ray diffraction studies. Swelling in the first stage is proportional to the power of the alkali-metal ion to combine with water, and inversely proportional to the size of the ion. This is so in the series Li, Na, and K. Alcoholic alkalis swell cellulose in proportion to the amount of water present in the system.

Variations in Structure of Cellulose in Alkaline Solutions. T. Petitpas. Mém. Services chim. État (Paris), 34, 139-147 (1948): Chem. Abs., 44, 7534 (25th Aug. 1950).

X-Ray diffraction studies were carried out on relaxed

ramie immersed in alkali for 15 hr. at 22°c. The fibres were then blotted free of excess solution and mounted under tension; the fibre was surrounded with a thin polystyrene reliably, the lore was surrounced with a third physylene sleeve to reduce evaporation. For the treated fibres—With 12-20% NaOH: a 13·5 A, b 10·3 A, c 12·9 A, β — 40°; 20–30% NaOH: a 9·5, b 15·2; LiOH < 11%: a 19, b 10·3, c 17·5, β — 30°. The lattice for cellulose treated with KOH was poorly defined and resembled that of mercerised cellulose.

Absorption of Caustic Soda from Alkaline Solutions by Native Cellulose—Formation of Alkali Cellulose. A. Breguet, R. Viatte, and H. Perra. Mém. Services chim. État (Paris), 34, 149–151 (1948): Chem. Abs., 44, 7534 (25th Aug. 1950).

Native cellulose was immersed in solutions of up to 27% NaOH at 20°c. The curve of absorbed NaOH plotted against concentration is concave up to 10·33% NaOH, convex from this point to 17·23%, and linear to 27%. Absorption in the first zone is by the amorphous portions only, that of the second zone progressively affects the crystalline portions with formation of the typical mercerised cellulose network, and in the third zone absorption occurs at the newly exposed OH groups. This is confirmed by X-ray studies. Formation of $(C_6H_{10}O_5)_2$, NaOH is postulated on entry into the third zone of absorption.

Heterogeneous Degradation of Cellulose. II—Mild Oxidative Degradation by means of Sodium Toluenesulphonsodiochloroamide [Chloramine-

T]. T. Kleinert and V. Möszmer. Sitzungsber. Öster. Akad. Wiss., 159, (1-2), 118-121 (1950).
A substance of 94·6% α-cellulose content, with a copper viscosity of 245, and an average degree of polymerisation (D.P.) as determined viscosimetrically of 785, has been degraded in very dilute chloroamine solutions over long periods of time (100–400 days). Decomposition occurred approximately linearly at D.P. 500, but was only slight at lower values.

Ultrasonic Disintegration of Cellulose Fibres before and after Acid Hydrolysis. F. F. Morehead. Text. Research J., 20, 549-553 (Aug. 1950).

When untreated cellulose fibres are subjected to ultrasonic vibrations they are broken down into fine fibres. If, however, the fibres are subjected to acid hydrolysis prior to exposure to ultrasonic waves, then "particles", many of which are obviously aggregates, are formed. Native cellulosic fibres always yielded much longer and larger crystallites than the regenerated fibres, and a close relation was noted between the observed length of the crystallites and the chain length as calculated from viscosity measurements. It is considered that the results support the theory that in acid hydrolysis of cellulosic fibres, the chains most subject to attack are those in the amorphous regions of the

Air Flow Method of Measuring the Specific Surface of Jute. M. M. Roy, R. R. Mukherjee, and M. K. Sen. J. Textile Inst., 41, T 249-T 254 (July 1950).

The air flow method for measuring specific surface has been applied to jute. The results, which agree with microscopic estimations, indicate a specific surface of about 1000 sq. cm./c.c. Tossa jute is in general slightly coarser than white jute.

Influence of Molecular Configuration on the Frictional Properties of Fibres. J. Lindberg and N. Gralén. J. Textile Inst., 41, T 331 (Aug. 1950).

Frictional properties of wool are considered in the light of recent theories that frictional properties of surfaces are dependent on the molecular attraction between the surfaces. Low with scale friction in wool is therefore attributed to the extremely inert epicuticle, whose removal or modification leads to an increased frictional value. Stress is laid on the importance of fibre surface properties in making specific materials from synthetic fibres. J. W. B.

Plasticity of Wool [and Sulphur Content]. O. Ripa and J. B. Speakman. Nature, 166, 570-571 (30th Sept. 1950).

Lincoln wool fibres are extended in water under constant load, and graphs drawn of log $(E - E_t)$ against t, where E_t is the extension at time t. It is found that the slopes k of the straight lines so obtained vary widely, and after dividing a large number of fibres into three groups

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according to their rates of extension, their S contents are determined. A similar wide variation in S content is found, and the value of $k \times (S \text{ content})$ is roughly constant, though only for the same type of animal fibre. J. W. B.

Isolation of an α - and β -Protein in Wool. P. Alexander and C. Earland. Nature, 166, 396-397 (2nd Sept.

Wool is oxidised with peracetic acid and, after oversion of 90% of the cystine to cysteic acid, conversion of 90% becomes freely soluble in dilute alkali apart from an insoluble residue of 7-10%. This fraction is a tubular membrane forming part of the cuticle, and has a β -keratin structure, whereas the alkali-soluble portion, isolated by precipitation with acid, has the structure of a-keratin. The soluble fraction has a mol. wt. of 70,000 and is soluble in solvents capable of breaking hydrogen bonds, e.g. formic acid, from which it is regenerated, and if desired oriented, in the a-form by dilution with water, or in the β -form by removing the formic acid by distillation in vacuo. It is concluded that the wool is polyphase in structure, the β -phase forming part of the cuticle and providing protection to the main bulk of a-protein. J. W. B.

Polycrystalline Structure of Wool. F. Happey.

Nature, 166, 397–398 (2nd Sept. 1950). Structural aspects of the problem discussed by Alexander and Earland (above) are considered, with emphasis on the X-ray data and the apparent connection between the β-keratin cuticle component and the unreactive nature of wool fibres. It is suggested that the solventprotein interaction may influence the final structure of the molecule. J. W. B.

Combination of Wool Protein with Cations and Hydroxyl Ions. J. Steinhardt and E. M. Zaiser. J. Biol. Chem., 183, 789–802 (April 1950). The titration curves of wool at 0°c. with 12 strong

monacid bases show similar wide differences with respect to position on a pH axis as have previously been found with acids. Thus, the affinity of cations for protein increases with increasing molecular dimensions. Among organic cations of the same weight, unsymmetrical ions produce much the larger displacement of the titration curve. Unlike the effects of anions, which are uniform over the entire acid curve, the effect of cations is more marked on that portion of the titration curve which is also affected by formaldehyde, viz. the part due to lycine. The maximum shift of this part of the titration curve, obtained with tetradecyltrimethylammonium, exceeds 2 pH units. Marked effects on other portions of the curve are shown only by unsymmetrical ions larger than the hexyltrimethylammonium ion. As with anions, the binding of cations is brought about by van der Waals forces, which have an opportunity to manifest themselves only when long-range (electrostatic) forces increase the probability of close enough approach. No specific chemical bonds are F. F. E.

Action of Lithium Bromide Solutions on Wool and the Rôle of Hydrogen Bonds. P. Alexander.

Melliand Textilber., 31, 550-555 (Aug. 1950). Wool fibres contract about 14% in hot LiBr solutions of concn. > 50%. If the time of treatment is < 2 hr. at 100°c., then the fibres quickly return to their original length when placed in water. Irreversible contraction is observed with times of treatment > 2 hr. and in acid or alkaline solutions of LiBr. Measurements of 30% index show that reversible contraction causes no fibre damage. Irreversible contraction is accompanied by damage, which measurements of cystine content show not to be due to disulphide bond hydrolysis. The action of LiBr is to break hydrogen bonds, unlike e.g. peracetic acid, which causes contraction by breaking of disulphide bonds; thus formation of lanthionine cross-links prevents contraction with peracetic acid, but not with LiBr solutions. X-Ray and double acid, but not with LiBr solutions. X-Ray and double refraction measurements show that LiBr treatment causes disorientation. With severe treatments which cause fibre damage the disorientation is so extensive that the original bonds cannot be reformed, and are replaced by weaker ones. On the other hand, it has been shown that contraction by disulphide bond hydrolysis does not affect the X-ray diagram; i.e. the crystalline regions of the fibre remain unaffected. It is concluded that the crystallites are linked by disulphide bonds, and that contraction may

be induced both by intermicellar action on these disulphide bonds and by intramicellar action on hydrogen bonds.

Amino Acid Composition of Silk Fibroin from the Mulberry and Oak Silkworms. E. P. Tsintsevich and M. M. Botvinik. J. Appl. Chem. (U.S.S.R.), 23,

750-753 (July 1950). The amino acid composition was determined for the fibroins of a mulberry silk from Central Asia and of oak silk from the Crimea. The effect of variations in nutritional conditions was examined. These results, and those of other workers on similar varieties of silk, are tabulated. Unlike mulberry silk, oak silk contains more alanine than glycine, viz. 34.6% and 19.1% respectively, the corresponding figures for the mulberry silk being 25.4% and A. É. S.

High-molecular Chemical Studies on Silk. I-Soluh-molecular Chelinian Students and pholisty of Sericin when Degumming Silk and pholisty of the Degumming Liquor, S. Ueno. J. Soc. of the Degumming Liquor, S. Ueno. J. Soc. Textile Cellulose Ind. Japan, 4, 81-86 (1948): Chem. Abs., 44, 7541 (25th Aug. 1950). In degumming silk with neutral (Marseilles) soap, the

loss m (%) is related to the amount of soap used c as follows—m = C/(a + bc), where a = 0.08233, b = 0.04540, follows—m = C/(a + c), where a = c volumes, a = c volumes, and C = const., the curve showing saturation at its inflection point at 25% soap. The solubility of seriein is related to the pH of the liquor as follows— $s = A(pH)^n + B$, where A = 0.03397, B = 0.6327, and n = 2.6853, B = 0.6327. varying with temp. and conen. Solubility increases rapidly from pH 7 to pH 8, where an inflection point appears, and thereafter slowly to pH 11, where the fibroin begins to dissolve. After the sericin has been dissolved, the pH shifts to the acid side, reaching a maximum acidity when the solubility is 18%. Before reaching this maximum, the sericin behaves as though ionised, owing to adsorption of soap ions, and beyond the maximum it behaves as an aggregate.

Dimensional Stability of Woollen and Worsted Fabrics, W. von Bergen and C. S. Clutz. Text. Research J., 20, 580-591 (Aug. 1950).

In the first part of the paper are described the main processes through which a piece of cloth goes to reduce relaxation shrinkage to a minimum and also the main steps this same cloth goes through in a tailoring shop. In the second part it is shown that the dimensional changes of wool fabrics can be attributed to (1) change in moisture content of the fabric, (2) relaxation shrinkage, and (3) strain due to external stresses. The inaccuracy of shrinkage test procedures is emphasised, and such a test can give a false indication of the performance of a fabric in practice. P. C.

Investigation on the Differences between Physical Properties of Skin and Core in Viscose Rayon. P. H. Hermans. Text. Research J., 20, 553-569 (Aug. 1950)

Using the topochemical acetylation technique of Elöd and Fröhlich (ibid., 18, 487 (1948): J.S.D.C., 65, 306 (June 1949)), the change in physical properties from skin to core of some typical viscose rayons has been examined. Degrees of peeling off the outer layers up to 60% and higher were realised, and the course of the reaction was meticulously controlled by applying dyeing tests to cross-sections. Density, birefringence, refractive index, swelling power, and mechanical properties were measured at different stages in the peeling-off process. Orientation and crystal-linity were followed by X-rays. In general, Elöd's results were reproduced, except that an increase instead of a decrease in density from skin to core was observed. Orientation remained constant for tyre cord rayon and decreased for textile rayon as peeling off proceeded. Considerable changes in strength and elongation occurred, but these are probably due to degradation by the acid catalyst used in acetylation.

Absorption and Fixation of Caustic Soda from Alkaline Solutions by Viscose Rayon. A. Breguet, R. Viatte, and H. Perra. Mém. Services chim. État

(Paris), 34, 153-155 (1948): Chem. Abs., 44, 7535 (25th Aug. 1950).

9-3% aq. NaOH gives maximum swelling of viscose rayon, and this coincides with maximum absorption of NaOH by the fibre. A secondary maximum of absorbed NaOH occurs at 21.9% NaOH, with a minimum at 14.0%. The first zone represents the nearly complete formation of an ionisable Na salt of cellulose. The minimum zone is ascribed to osmotic deswelling, whereas the second maximum and subsequent decline are due to rearrangement of secondary valency forces. The compound $(C_6H_{10}O_5)_2$, NaOH is thought to exist in the zone between the two maxima. C. O. C.

Separation of Cellulose into Molecules and Larger Particles during Esterification. R. Signer, A. Aeby, F. Opderbeck, and H. Studer. Sitzungsber. Öster. Akad. Wiss., 159, (1-2), 232-238 (1950). It is shown by means of the electron-microscope, the

It is shown by means of the electron-microscope, the ultra-centrifuge, and double refraction data that many cellulose esters of organic acids contain easily orientable macroparticles alongside chain molecules. The former can be concentrated by fractionation, identified from the sedimentation diagram, and rendered visible by the ultra-microscope. There are 6 illustrations.

H. H. H.

Viscosity and Molecular Weight of Macromolecular Solutions. H. Mark. Sitzungsber. Oster. Akad. Wiss., 159, (1-2), 140-151 (1950).

The viscosity number A and the molecular weight M of macromolecular substances are found to be related by the general equation $A = KM^n$, where K and a depend on the temperature and nature of the solvent. A theoretical analysis of the viscosity number is given, and data for the following solutions at 25° G, are included—cellulose in cuprammonium solution ($K = 0.85 \times 10^{-4}$ and a = 0.81), cellulose acetate in acetone (1.49 and 0.82), and cellulose acetate—butyrate in acetone (1.37 and 0.83).

(Calcium) Alginate Rayon. P. A. Koch. Textil-Rund., 5, 323–325 (Aug. 1950).

A review of the literature, with 44 references, dealing

A review of the literature, with 44 references, dealing with the discovery, development, production, chemical constitution, physical and chemical properties, and applications of alginate rayon.

B. K.

Improvement in the Stability to Water and Boiling of Casein and other Protein Fibres. H. Brintzinger and H. Wolff. Kolloid-Z., 118, 28-32 (July 1950). The water absorption and resistance to boiling of

and H. Wolff. Kolloid-Z., 118, 28–32 (July 1950).

The water absorption and resistance to boiling of synthetic and natural protein fibres can be improved by treatment with certain metallic salts. Experiments are described showing the effect of Cr compounds (one- and two-bath processes), potassium titanium oxalate, and the sulphates of La, Zr, Th, and Al. The last two compounds are not as effective as the other products mentioned.

B. K.

Influence of Molecular Structure on Swelling of Textile Fibres, S. Simmens and F. Howlett. J. Textile

Inst., 41, T 195-T 196 (May 1950).

Additional data are given to those presented by Abbott (ibid., 41, T 53 (Jan.-Feb. 1950)) showing that the axial swelling of nylon in water can be greater than its lateral swelling. When cellulose acetate rayon is immersed at 25°c. in 2% phenol the fibre at first swells rapidly and then shrinks transversely while swelling considerably axially. The influence of the "skin effect" may be contributory to this phenomenon.

H. K.

[Influence of Molecular Structure on the Moisture Absorption and Swelling of Nylon Filaments.] M. V. Forward and H. J. Palmer. J. Textile Inst., 41, T 267-T 268 (July 1950).

Comments are made on the observations reported by Abbott and Goodings (ibid., 40, T 232-T 246 (1949): J.S.D.C., 66, 246 (April 1950)) on the moisture regain and swelling of nylon filaments. Increase in moisture regain after water and ethanol treatments may be due to removal of anti-static finish. Decrease in moisture regain after reatment with other swelling agents may be due to removal of low-mol.wt. material and the difficulty of eliminating e.g. m-cresol from the nylon. It is agreed that, for low degrees of swelling, the swelling anisotropy of yarns does not bear a simple relationship to their degree of orientation. Water vapour causes isotropic swelling of drawn nylon because the water is absorbed only in regions of low interchain bonding energy. These regions are subject to a change in orientation during pretreatment of the yarn with water. It is misleading to regard undrawn nylon yarn as isotropic, since orientation and

strain are introduced during manufacture, and a skin effect has been noted by Preston (*ibid.*, 41, x 126 (1950)). Since the skin is absent from drawn yarn, it is probably broken during drawing.

F. A.

Mechanical Properties of Perlon. G. Metzger and F. Sauerwald. Kolloid-Z., 117, 176–180 (June 1950). A special polyamide filament was prepared containing two coloured cylindrical layers co-axial with the fibre axis; cross-sections of the fibre thus showed concentric rings. The diameters of the rings in sections from drawn and undrawn portions of the same filament showed that the deformation on stretching is distributed uniformly across the section. Viscosimetric measurements of degree of polymerisation showed no difference between the drawn and undrawn portions. Perlon castings with improved mechanical properties were obtained by the pressing at 100–160°c. of bundles of Perlon filaments which had first been dipped in a solvent to swell the surface of the filaments.

New Inorganic Fibre Crystal. L. Ebert and R. Fiala. Sitzungsber. Öster. Akad. Wiss., 159, (3-4), 414-418 (1950).

(1950). The compound Na₂Sb₄S₇,2H₂O is found to form a saturated mixed crystal with ~ 0·4 Na₂S of composition Na₂,₈Sb₄S_{7·4}, which is macroscopically different from the initial substance, and which the electron-microscope indicates to possess a fine fibre structure of ~ 100 A. diameter. It is concluded, after a detailed discussion, that fibre structures may be expected in oxygen and sulphur containing polycomplexes, if the O or S content is decreased by about one-twelfth from that possessed by the corresponding simple infinite meta-chain compound.

PATENTS

Water-sensitive Cellulose Derivatives and Fibres therefrom. J. P. Hollihan, S. A. Moss, and American Viscose Corpn. U.S.P. 2,511,060.

Acrylonitrile is added to viscose and the mixture left until all the cyanoethyl groups introduced by direct reaction between the acrylonitrile and the cellulose xanthate are hydrolysed to carboxyethyl groups, i.e. until N is not detectable by ordinary analytical procedures. Fibres formed from the resulting carboxylated cellulose are more highly reactive than other cellulosic fibres and are water-sensitive, this sensitivity being accurately and reproducibly predetermined within wide limits depending upon the proportion of carboxyethyl groups to anhydroglucose units of the cellulose. They are useful as scaffolding yarns which may be subsequently dissolved out by simple treatment with water. C. O. C.

Highly Twisted Crêpe Yarn of Organic Derivatives of Cellulose. British Celanese Ltd. B.P. 642,333. Sizing the yarns with a water-soluble ester of an organic acid before imparting the crêpe twist yields yarns which, when made up into fabric and then given a hot aqueous treatment, yield a given degree of crêpe with less twist

than if the sizing had been omitted. C. O. C.

Differential Colour Effects in Fabrics. C. Dreyfus,
A. Schwartz, and Celanese Corpn. of America.

U.S.P. 2,507,561.

By imparting differences in twist along the length of a non-filamentary yarn, cross-dyed or mottled effects are obtained on subsequent dyeing, as the portions of lower twist are dyed deeper than those of higher twist. C. O. C.

Papermakers' Felt. R. J. Lee. B.P. 642,788. Strong felt blankets with increased operational life comprise woven and fulled fabric having warp and filler yarns, one of which forms a substantial part of the felt surface and one or both of which contain ramie fibres, some of which must be exposed on the surface, to the extent of 5-95% by wt. of felt.

Papermakers' felt blankets comprise wool fibres and 5-85% by wt. of plastic fibres, which are made from a vinylidene chloride-vinyl chloride copolymer containing < 10% of plasticiser, stabiliser, pigments, etc. J. W. B. Fabricated Sheets of Unspun Fibres. Fibre Products

Laboratories Inc.

Laboratories Inc.

Unspun fibres, preferably of long staple and including types not normally spinnable, e.g. kapok or Spanish moss,

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iscose ion of sorbed are arranged in a web and oriented by a succession of carding and drawing processes. One or several webs are bonded by interdeposition, e.g. by spraying at a number of intermediate stages, of 20--50% of thermoplastic material, e.g. asphalt, cellulose ethers or other resins, and passing over or between heated rollers to produce the necessary adhesion.

Cellulose Sulphate. J. C. Thomas and Du Pont. (III, p. 650.)

Gloss Measurements on Fabrics. R. G. Quynn, E. J. Bernet, and E. K. Fischer. (XIV, p. 665.)

VII—DESIZING; SCOURING; CARBONISING; BLEACHING

PATENTS

Preventing Linting in Dry Cleaning. J. W. Kennedy, P. M. Rapier, and Great Lakes Carbon Corpn. U.S.P. 2,503,744.

Addition to the solvent of a minute quantity of an oilsoluble Mg, Ca, Zn, Sr, Cd, or Ba cleate renders it conductive to such a degree that linting is wholly prevented.
These heavy-metal scaps are not removed from the solvent
by the work nor by diatomaceous earth filters, and the
conductivity imparted by them persists through repeated
use and filtration.

C. O. C.

Stripping Colour from Wool, etc. M. Harris, A. E. Brown, and Harris Research Laboratories.

 $U.S.P.\ 2,508,714.$ Wool is stripped by treating it with a reducing agent for keratin in presence of an alkylene dihalide, preferably at 60–100°c. and pH >7 in a bath containing 3–100% of reducing agent and >0.00045 mole of the alkylene dihalide per gram of keratinous material. The stripped fibres are resistant to oxidising, reducing, and alkaline agents, and have practically the same physical properties as the unstripped fibres. C. O. C.

Standard Scouring Process for Loose Wool. Schweizerischer Verband für die Materialprüfungen

der Technik, Kommission 25. Richtlinienblatt A 2102. (XIV, p. 666.)

Standard Scouring Process for Wool containing Carding and Spinning Oils. Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25, Richtlinienblatt A 2103. (XIV, p. 667.)

Rapid Method for Control of Wool Scouring. M. Robinet. (XIV, p. 667.)

VIII- DYEING

Effects of Yarn Irregularity in Dyeing and Finishing.
R. G. Fargher, H. M. Taylor, and F. W. Thomas.
J. Textile Inst., 41, P 590-P 608 (July 1950).
The influence of various types of yarn irregularity on

the processing of cotton and spun rayon fabrics is discussed. Softer portions of warp yarn take up more size than harder portions and retain this size more tenaciously during desizing. Residual size caused by yarn irregularity has a pronounced effect on the handle of spun rayon In dyed goods the extent of streakiness caused by weight irregularity depends on the structure of the fabric: it is most apparent when the threads are not quite touching and decreases with either increase or decrease in the spacing of the threads. Twist variations in the west yarn of a fabric affect the rate of raising and the appearance of the raised cloth. Changes in the natural colour of cotton weft yarns have been found to be associated with differences in the reducing power of the cotton after thorough washing. Differences in the extent to which grey cottons mildew or darken on heating are due to differences in their water-soluble constituents, particularly those of a reducing character. Shade variations in bleached and dyed cottons may be caused by differences in their contents of non-cellulosic matter, which are detected by staining with Methylene Blue. F. A.

Fundamental Investigations and Bulk Application of Vat Dyes. Joachim Müller. Textil-Rund., 5, 261–269 (July), 303–315 (Aug.), and 439 (Oct. 1950). The various factors influencing the behaviour of leuco

compounds of anthraquinonoid vat dyes, especially Indanthren Blue RSN (indanthrone) are discussed. These include crystallinity, dehalogenation, under-reduction, over-reduction, soaping-off, purity, particle size (on fibre), and enol-keto tautomeric change. The amount of NaOH, conen. of leuco vat, temp., and additions such as Turkey Red oil and surface-active agents, including Nekal BX and Igepon T (IG) as well as sulphonated fatty alcohols, can all affect the final results. The effect of variations in the soaping-off process on the subsequent fastness properties, such as chlorine, are discussed. The influence of variations in time and temp. on the affinity of Indanthren Red FBB on Perlon, cotton, Vistra, and cuprammonium rayon is given in graphical form.

B. K.

Recent Progress in Dyeing Silk and Rayon. [G. T.] Douglas. Teintex, 15, 357-367 (Aug. 1950). Silk can be dyed in cheese form, under neutral con-

Silk can be dyed in cheese form, under neutral conditions, using acid milling dyes. These dyes may also be used for dyeing the silk in silk-nylon mixtures in presence of a reserving agent for the nylon. Direct dyes can be applied to viscose fabric by padding with a conc. dye solution and then fixing the dye either by steaming or by treating in a boiling salt bath. The application of vat dyes to viscose packages by the Abbot-Cox process, and also of chrome dyes to nylon, is described.

F. A.

Measurement of Dyeing Properties and Correlation with Orientation in Nylon Yarn. A. R. Munden and H. J. Palmer. J. Textile Inst., 41, p 609-p 634 (July 1950).

The dveing characteristics of nylon yarns of different states of orientation have been measured using Durazol Blue 2R (ICI), which preliminary experiments showed to be very sensitive to changes in orientation, and Solway Blue B (ICI) and Duranol Brilliant Blue BN (ICI), which have covering properties typical of acid and dispersed acetate dyes respectively. With Durazol Blue 2R dyeing rate decreases with increase in orientation, the rate of decrease being greater at the higher degrees of orientation. Solway Blue B and Duranol Brilliant Blue BN behave qualitatively in the same manner, but with these dyes the reduction in dyeing rate with increase in orientation is less. A simple test for detecting variations in the orientation of a nylon yarn consists in dyeing a length of knitted fabric under standard conditions with Durazol Blue 2R. Any streakiness is assessed against that in dyeings on standard fabrics knitted from yarns with known short-period orientation differences.

F. A.

Vat Dyeing of Polyamide and Polyurethan Fibres. Joachim Müller. Melliand Textilber., 31, 564-569 (Aug. 1950).

The affinity of polyamide and polyurethan fibres for vat dyes is increased by steaming. The light fastness of the dyeings is increased by the steaming treatment and also by complete oxidation and soaping. With careful selection of dye and dyeing method a useful degree of fastness may be obtained with the vat dyes.

F. A.

Physical Conditions for Penetration of Dyes into Vegetable Tissues. W. Kopaczewski. Ann. Inst. natl. Recherche agron., Ser. A, Ann. agron., 1, 26-40 (1950): Chem. Abs., 44, 7390 (25th Aug. 1950). An electrocapillary analysis of the penetration of dyes into filter paper and giant white daisies. Only acid dyes

An electrocapillary analysis of the penetration of dyes into filter paper and giant white daisies. Only acid dyes and some indicator dyes but no basic dyes penetrate into daisies. Only highly dispersed and dialysable dyes penetrate into vegetable tissues; no colloids, even electronegative colloids, penetrate. Dialysable or slightly dialysable dyes, acid or electronegative, which are strongly adsorbed by animal charcoal, do not penetrate easily into the tissues. There is close analogy between the coloration of white flowers and the penetration of dyes into the capillaries of filter paper, except for some details in the behaviour of the ions.

C. O. C.

Studies on Japanese Dyeing Tannins. XXIII— Influence of Volume on the Absorption of Various Tannin Extract Solutions by Cellulose. Y. Veda and Y. Ogawa. J. Soc. Chem. Ind. Japan, 44, Suppl. Binding 253–254 (1941): Chem. Abs., 44, 7541 (25th Aug. 1950).

Absorption by cotton of Japanese sumach, fustic, and catechu from 4% solutions during 24 hr. was determined at 15, 25, and 30°c. The results were plotted both directly

te

and logarithmically as percentage of absorbed tannin versus vol. of tannin soln. Absorption is inversely proportional to the liquor ratio and increases with decrease in temperature.

 $\begin{array}{c} \textbf{Dyeing Animal Hairs with Anthraquinone Vat Dyes.} \\ \textbf{A. E. Weber and Allied Chemical \& Dye Corpn.} \\ \textbf{U.S.P. 2,508,203.} \end{array}$

Animal hairs can be dyed with little degradation by using vate at pH 12-13 which contain excess of alkalimetal hydrosulphite and controlled quantities of a neutral alkali-metal salt. The amount of salt to be used varies from 0.5 to 50.0 g./litre according to the dye used.

C. O. C. Coloration of Cellulose Esters or Ethers. H. C. Olpin and T. Jackson.

B.P. 641,835.

In dyeing cellulose esters or ethers with esters of leuco vat dyes and polybasic acids from a mixture of water and an organic liquid, adding urea to the dye liquor and steaming the impregnated material result in better colour In addition, the hues obtained more nearly approach those the parent vat dyes yield when dyed on cellulose by conventional methods.

Colouring Secondary Acetone-soluble Acetate Rayon.
G. D. Sutton and T. E. Marchington & Co. Ltd.
B.P. 641,875.

Modification of B.P. 622,676 (J.S.D.C., 65, 466 (Sept. 1949)). Much more stable dye liquors are obtained if formamidinesulphinic acid, or a solution of sodium hydrosulphite stabilised at pH 10·5–11·4, is used as the reducing agent. The formamidinesulphinic acid may be added as such to the dye liquor or may be formed in situ in the dye liquor by oxidising thiourea with hydrogen peroxide. The hydrosulphite solution can be stabilised with calcium cyanamide or hydroxide.

C. O. C.

Dyeing Cellulose Esters or Ethers without Dyeing Superpolyamides. H. C. Olpin and D. L. Bell. B.P. 642,840.

Cellulose esters or ethers can be dyed in presence of superpolyamide fibres without the latter becoming coloured by using a dye which has affinity for the superpolyamide when applied from an aqueous bath dissolved in a liquid which acts as a swelling agent for the cellulosic fibre but not for the superpolyamide; e.g. a nylon 66 warp-acetate rayon weft fabric is immersed for 5 min. at 25°c. in 2100 c.c. methylated spirits, 720 c.c. water, 90 c.c. acetic acid, 60 g. sodium thiocyanate, 3 g. 1-phenylamino-anthraquinone, and 0.2 g. 2-nitro-4-chlorodiphenylamine, when the acetate rayon is dyed deep pink but the nylon is left unstained. C. O. C.

Pad Dyeing of Cellulose Derivative Fabrics with an Alcoholic Solution followed by Padding with an Aqueous Thiocyanate Solution. C. M. Croft, T. S. Waller, and Celanese Corpn. of America.

U.S.P. 2,511,103. Deep, fast, and level dyeings are rapidly obtained by first padding with an aqueous alcoholic dye liquor and then with a concentrated aqueous solution of an inorganic

Pad Dyeing of Fabrics made from Sized Spun Staple Fibres of an Organic Derivative of Cellulose followed by Desizing. W. T. Normand and Celanese U.S.P. 2,511,938. Corpn. of America.

Fabrics containing staple fibres of an organic derivative of cellulose sized with a proteinaceous size are dyed level, even, and free from overdyed surface fibres by padding them in an aqueous alcoholic dyebath containing an inorganic swelling agent and then souring the dyed fabric to desize it. C. O. C.

Differential Colour Effects in Fabrics. C. Dreyfus, A. Schwartz, and Celanese Corpn. of America. (VI; p. 659.)

IX-PRINTING

Chemical Constitution versus Printing Performance and Other Properties of Vat Dyes. L. D. Barrick. Amer. Dyestuff Rep., 39, P 324-P 328 (15th May 1950).

In general, a vat dye having good printing properties is suitable for all other applications, including conversion to the leuco sulphuric ester. Nearly all satisfactory vat printing dyes have a compact polynuclear ring system with one pair of reducible quinone or carbonyl groups. Simple substituents, such as Hal, CF₂, CH₃, O·CH₃, and O·C₂H₅, may affect the hue and other characteristics of the dye, but seldom inhibit printing performance. In fact, they may improve it. Larger groups, such as benzoylamino and anthraquinonylamino, as well as molecules containing multiple quinone systems, tend to inhibit printing performance. Finally, for brilliance of shade and consistency in dysing and printing behaviour, it is preference in dysing and printing behaviour, it is preference. consistency in dyeing and printing behaviour, it is preferable to choose a molecule having a symmetrical, compact polynuclear ring structure which functions as a single A. S. F.

Direct Printing of Aniline Black on Rayon — Reduction of Fibre Damage and Prevention of Greening. W. Schramek. Melliand Textilber., 31, Greening. W. Schr. 571-575 (Aug. 1950).

Minimum damage and greening when printing Aniline Black on rayon by the steam process are obtained by (1) reduction of the concn. of aniline salt to 70 g. per kg. of printing paste, (2) addition of organic acids, preferably acetic acid, (3) use of an optimum amount of potassium ferrocyanide, and (4) addition of up to 20 g. of ammonium thiocyanate per kg. of printing paste.

PATENTS

Pigment Binders. F. G. La Piana, G. N. Houth, and Stein, Hall & Co. Inc. U.S.P. 2,511,113. A binder, which secures insoluble pigments on fabrics so that the prints are fast to light, washing, and rubbing and which does not impair the handle of the fabrics, comprises a polyvinyl or polyvinylidene resin containing Cl, preferably in combination with a plasticiser, e.g. synthetic latex, and a water-soluble thermosetting urea-formalde-hyde resin. This binding composition is readily thinned with water and readily washed from machinery. C. O. C.

Printing or Dyeing Superpolyamide Fibres. Ciba Ltd. B.P. 642,837.

The material is printed or padded with a composition comprising an ester salt of a leuco vat dye, an acid-liberating agent, and as an oxidising agent a nitroaryl-sulphonate, and is then aged as usual.

C. O. C.

Printing on Polyvinyl Resins. L. W. E. Townsend and Associated Technical Manufacturers Ltd.

The essential feature of a permanent printing ink for use on polyvinyl chloride is that it contains a resin compatible with the polyvinyl chloride with or without compatible plasticisers and solvents, some of which are solvents for polyvinyl chloride. C. O. C.

Diazotype Materials stabilised with Sulphoamino-benzoic Acids. General Aniline & Film Corpn., W. H. von Glahn, and L. N. Stanley. B.P. 642,992. Diazotype materials are stabilised to decomposition of

the diazo compound and premature coupling by incorporating a sulphoaminobenzoic acid or an N-substituted derivative thereof. C. O. C.

Diazotype Compositions containing p-N-Hydroxy-ethylamino-o-methylbenzenediazonium Com-pounds. General Aniline & Film Corpn., W. H. von Glann [sic], and L. N. Stanley. B.P. 642,422.

The precoupling stability of diazotype layers for either final reproduction work in deep tones or intermediate transparency work in sepia or other ultraviolet-opaque tones is greatly improved by using as the light-sensitive component diazo derivatives of compounds of formula-

 $(R = H, CH_2, C_2H_5, or C_2H_4OH).$

Diazotype Material. General Aniline & Film Corpn., S. C. Slifkin, and H. C. Unkauf. B.P. 643,375. Use of a light-sensitive compound of formula—

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(R1 = H, Alk, or hydroxyalkyl; R2 = Alk or hydroxyalkyl; X = Alk, Alk.O, hydroxyalkyl, or COOH) with a coupler of formula-

 $(W = H, [CH_2]_n COOH, Alk, or hydroxyalkyl; Y = H, SO_3H, or a salt of the latter; Z = H or <math>CH_2 \cdot NH_2$; when W = H either Y or Z must be other than H) yields dye images of high actinic opacity.

Diazotype Materials. General Aniline & Film Corpn. and T. J. Trojnar. B.P. 643,063.

Incorporation in diazotype compositions of a lustrous powdered metal pigment minimises discoloration of the prints on exposure to sunlight or ultra-violet radiation. In addition the contrast of the images is controllable within wide limits to yield softened highlights and open shadows, as well as a wide range of control of gloss, C. O. C.

Developer for the Positive Diazotype Process.

Chemische Fabriek L. van der Grinten. B.P. 643,309.

Aqueous developers for the positive diazotype process

contain an azo coupling component, an alkali borate, and a water-soluble organic polydroxyl compound having not < 3 alcoholic hydroxyl groups attached to adjacent carbon atoms, which enhances the solubility of the borate.

Half-tone Photomechanical Screen Printing.
D. Walker and David Evans & Co. Ltd. B.P. 641,545. Elimination of moiré effects when printing in more than one colour is obtained by using a screen having 60-200 meshes/in. and having half-tone areas of different sizes and other areas which have been rendered impervious to colouring matter, both sets of areas having been obtained by light-hardening a photosensitive material and dissolving away that part of it which has been unaffected by light.

Nylon and Cellulosic Yarn Patterned Fabric. H. L. Huey, W. W. Russell, and Sayles Finishing Plants Inc. (X, p. 663.)

X-SIZING AND FINISHING

Systematic Chemistry of Textile Finishing. Sitzungsber. Öster. Akad. Wiss., 159, (1-2),

260-265 (1950).

This paper is based on a lecture to the American Chemical Society on 29th March 1949, in which the author proposed a topological and scientific study of recent new processes for the improvement of textiles. The former would distinguish between processes which occur within the separate fibres, between the fibres, or between the yarns. The latter would distinguish various mechanisms of fixing the finishing materials employed, viz. (1) by previous destruction and restoration of the cohesion of the fibre material or of the finishing agent; (2) by adhesion of the agent to the fibre by means of subsidiary or main valency forces. н. н. н.

Manufacture and Testing of Absorbent Cotton [and Other Fibres]. E. Cerbaro. Boll. cotoniera, 37, 247-250, 366, 367 (1942): Chem. Abs., 44, 7535 (25th

Aug. 1950).

Methods of manufacture of absorbent cotton and other fibres are described, as well as standards and methods of test based on German practice. The mean fibre length should not be < 20 mm. and ash content not > 0.3%; should not be <20 hin. and as solicing 50 g. of heat storilised wadding with 150 c.c. of $\mathrm{CO_3}$ -free water should give no reaction for SO_4^{z-} or Cl^- , should be neutral to phenolphthalein, and almost clear and colourless. Water absorbency is assessed by the rate at which a compressed ball of wadding sinks when placed on water (Moser's method). The degree of degradation (Schwalbe's method) should not be > 0.5 and 1.25 for non-sterilised cotton and viscose rayon respectively, corresponding figures for sterilised fibres being 0.65 and 1.40.

Mercerisation of Textiles containing Spun Viscose Rayon—Identification of Mercerised Viscose Rayon. E. Cerbaro. Boll. cotoniera, 36, 453-456

(1941): Chem. Abs., 44, 7535 (25th Aug. 1950).
Viscose rayon swells when mercerised with aq. NaOH, and the characteristic longitudinal striations, normally parallel to one another and the long axis of the fibre, tend to be displaced and to run diagonally across the fibre, and 'to converge and diverge. This method may be used, in conjunction with dye-affinity tests, to identify mercerised viscose rayon; photomicrographs illustrating the effect The fibres should be mounted in glycerol or are given. cedar wood oil; the I2-ZnCl2 reagent should not be used, as this itself causes the fibre to swell. Methods of mercerisation are described. C. O. C.

Plastic Treatment of Rayon. N. Saito. Teifin Times (Japan), 20, (6), 1, 2 (1950): Chem. Abs., 44, 7541 (25th Aug. 1950).

Ordinary rayon yarn treated with thermoplastic and thermosetting plastics together with a cationic reagent in a mixed colloidal state, and then cured for 1-15 min. at 130°c., showed higher wet strength and higher elongation at break than either untreated yarn or urea-formaldehydetreated varn.

Titanium Compounds as Fire-retardant Agents for Fabrics. I. M. Panik, W. F. Sullivan, and A. E. Jacobsen. Amer. Dyestuff Rep., 39, 509-516 (7th

Although titanium compounds have not been widely used for imparting flame resistance to cotton fabrics, it is shown that it is possible to obtain moderate flame resistance by the deposition of titanium dioxide alone; but glow retardance and resistance to leaching and to laundering The use of titanium and antimony oxides together, however, gives relatively permanent flame- and glow-retardant properties, much better than those obtained by using either separately. Application is by impregna-tion in a solution of titanium chloride-acetate and antimony trichloride, followed by partial drying, treatment in ammonia solution, and rinsing. For optimum results the ratio $\mathrm{Sb}_2\mathrm{O}_3:\mathrm{TiO}_2$ should be >0.9 and the deposition of ca. 15% of the mixed oxides is necessary. Better results are obtained by precipitation with ammonia than with the other alkalis tried. W. K. R.

Studies on the Microbiological Degradation of Wool Digestion of Normal and Modified Fibrillar
 Proteins. W. H. Stahl, B. McQue, G. R. Mandels, and R. G. H. Siu. Text. Research J., 20, 570-579

(Aug. 1950).

The susceptibility towards digestion by the fungus Microsporum gypseum of various fibrillar protein fibres has been examined. Collagen had the lowest resistance, followed by feather, hoof, wool, horn, horsehair, mohair, and silk in increasing order. Chemical constitution and fibre molecular structure are the two main factors governing rate of digestion, whilst in keratins the degree of polymerisation is the most important. The histological complexity and geometric structure of keratinaceous tissues are not important factors in determining rate of

Occurrence of a Network in the Excrement from the Larva of the Clothes Moth. G. Lagermalm, B. Philip, and N. Gralén. Nature, 166, 484-485 (16th Sept. 1950).

Electron-microscopic examination of disintegrated wool from clothes-moth larvæ excrement reveals regular fibrous networks, which are considered to originate in the larvæ intestines as they are also produced by larvæ fed on a wool-free diet. J. W. B. on a wool-free diet.

PATENTS

Yarn Sizing. Monsanto Chemical Co. B.P. 643,273. An ammonium or alkali-metal salt of a copolymer of styrene or a substituted styrene with maleic anhydride (2–15% by wt.) is applied from aqueous solution as the sole sizing agent. The sized yarn weaves well without dusting, and the resultant fabric has a semi-permanent stiffened finish. It is unnecessary to desize before dyeing and finishing. C. O. C.

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Treating Cellulose Fibres with Alkali Metal Hydroxide and Copper-Alkylolamine Complex. T. C. Whitner and Chemical Laboratories Inc.

U.S.P. 2,512,558.

Addition of alkali-metal hydroxides to the aqueous hydroxyalkylamine-copper complexes of U.S.P. 2,466,682 (cf. J.s.D.c., 65, 316 (June 1949)) increases or promotes their action on cellulosic fibres: e.g. the presence of 4% alkali-metal hydroxide decreases the affinity for dyes as compared with fibres treated in absence of the hydroxide; it seeds to be a support of the compared with fibres treated in absence of the hydroxide; it seeds the compared with fibres treated in absence of the hydroxide; it seeds the compared with fibres treated in absence of the hydroxide; it was the compared with fibres treated in absence of the hydroxide; it was the compared with fibres treated in absence of the hydroxide; it was the compared with fibres treated in absence of the hydroxide; it was the compared with fibres treated in absence of the hydroxide; it was the compared with fibres treated in absence of the hydroxide; it was the compared with fibres treated in absence of the hydroxide; it was the compared with fibres treated in absence of the hydroxide; it was the compared with fibres treated in absence of the hydroxide; it was the compared with fibres treated in absence of the hydroxide; it was the compared with fibres treated in absence of the hydroxide; it was the compared with fibres treated in absence of the hydroxide; it was the compared with fibres treated in absence of the hydroxide; it was the compared with the compar if > 4% hydroxide is used, then a mercerising effect is obtained.

C. O. C.

Rendering Wool Unshrinkable. R. Bloch, L. V. Farkas, K. Goldschmid, M. Lewin, I. Schnerb, and P. Goldschmidt. U.S.P. 2,508,007.

The wool is treated in an aqueous liquor containing free HCl and water-soluble bromate over and above the amounts of acid and bromate ion liable to be absorbed by the wool, the treatment being so controlled that 6.4-16.0 g. of bromate ion is consumed per kg. of air-dry wool. The process can be combined with milling by using as the milling liquor hydrochloric acid in excess of that absorbed by the wool and bromate to at least the amount absorbed by the wool, and when the desired amount of milling has occurred adding enough bromate to obtain the unshrinkable finish. C. O. C.

Improving the Chemical and Physical Properties of Keratinous Material. M. Harris, A. E. Brown, and Harris Research Laboratories. U.S.P. 2,508,713. Treatment of wool or the like with a reducing agent in presence of formaldehyde, preferably at pH 3-9 and 60-100°c., replaces the disulphide bonds of the keratin by

alkylene cross-linkages which are resistant to oxidising, reducing, and alkaline agents without affecting the mechanical properties of the fibres. C. O. C.

Improving the Liveliness, Fullness, Crease-resistance, Solvent-resistance, Melting Point, and Affinity for Dyes of Heat-set Fabrics containing Oriented Nylon Yarns. I.C.I. Ltd. B.P. 640,960.

A heat-set fabric containing nylon fibres in which the nylon contains H-bearing amide groups is impregnated in absence of alcohols with an inorganic or organic compound whose sat. aq. soln. has $\mathrm{pH} < 3$ and then, while maintained at fixed dimensions, treated in absence of water with formaldehyde vapour at $100-250^{\circ}\mathrm{c}$. until the nylon contains at least 0.5% by weight of combined formalde-

Heat-stabilised Nylon. H. W. Gray and Du Pont. U.S.P. 2,510,777.

Incorporation of a small amount of hypophosphorous acid, an inorganic hypophosphite, an alkylor arylphosphinic or -phosphonous acid or a salt or ester thereof increases the stability of nylon to loss in strength and discoloration on heating. Nylon fabrics impregnated with a 0.5-5.0% solution of one of these compounds can be set and finished at 215-230°c. C. O. C.

Arylmercuric Compounds for rendering Nylon Self-sterilising. G. F. D'Alelio, H. D. Addison, and Pro-phy-lac-tie Brush Co. U.S.P. 2,507,299. Nylon impregnated with an arylmercuric compound in presence of nitric acid remains bacteriostatic throughout its useful life. C. O. C.

Nylon and Cellulosic Yarn Patterned Fabric. H. L. Huey, W. W. Russell, and Sayles Finishing Plants U.S.P. 2,509,146.

Nylon is woven with yarns chemically different from it. The fabric is treated all over or in patterns with chemicals which remove at least one of the sets of nonnylon yarns while not affecting nylon and, if desired, other non-nylon yarns present. C. O. C.

Figured Effects on Fabrics containing Superpolymer Fibres. C. Bener. B.P. 643,386.

A fabric containing as one of its components super-polymer fibres in the form of a pattern and at least one other kind of fibre is treated with an agent which causes the latter to swell but is not a swelling agent for the super-C. O. C. polymer fibres.

Waterproofing Textiles. M. J. Scott, S. H. Rider, and Monsanto Chemical Co. U.S.P. 2,509,174. Textiles are impregnated with an aqueous emulsion of

an aldehyde-aminotriazine condensate etherified with (1) 5-2 mol. of a sat. unsubst. monohydric aliphatic alcohol of 1-6 C and (2) 1-4 mol. of an unsubst. monohydric sat. or unsat. aliphatic alcohol of 12–30 C, and then heated at 100–300°c. The 100% water-repellency imparted by these resins to cellulosic and proteinaceous materials is resistant to repeated washings or dry cleanings. They neither discolour nor generate acidic materials on long ageing, nor do they alter the physical characteristics of the material treated. Nylon and other fabrics treated with the resins do not mark off.

Water-soluble Siliconates—Water-repellent Agents.
J. R. Elliott, R. H. Krieble, and General Electric U.S.P. 2,507,200.

Treatment with compositions containing water-soluble siliconates imparts the same desirable water-repellent properties as are obtained by treatment with organosilicon halides, and in the case of cellulosic materials results in little or no loss in strength. C. O. C.

Water-repellent Finish. F. J. Sowa. B.P. 643,458. Fibres of all types are rendered water-repellent by applying a compound of formula $R_y SiX_z$ (R = an organic radical; X = Hal or O-Alk; y and z = 1-3 and y+z=4) or a silanol derived from such a compound y+z=4) or a small distribution of the hydrolysing and/or polymerising it to form a water-insoluble polysiloxane. C. O. C. water-insoluble polysiloxane.

Mothproofing. Merck & Co. Inc. B.P. 642,248.

A mothproof fast to washing is obtained by the use of a water-soluble silicofluoride and a vinyl acetate resin either in that order or simultaneously from a solution or emulsion containing the two components.

Multi-ply Semi-stiff Fabric. Du Pont. B.P. 643,206. An undissolved, ungelatinised vinyl halide resin is dispersed in a plasticiser to produce a dough-like mass. This is then used as the adhesive for coating an interlining fabric, which is then united with other fabric by the use of pressure and sufficient heat to fuse the adhesive. C. O. C.

Metallic Coatings on Non-metallic Materials, G. J. Kmecik. U.S.P. 2,511,472.

Non-metallic materials, e.g. textiles or plastics, are coated with silver by applying an organic solvent solution of a silver salt, e.g. AgClO₄ in toluene, and then reducing the silver salt.

Reaction of Cellulose with Alkalis. G. Petitpas. (VI, p. 657.)

Absorption of Caustic Soda from Alkaline Solutions by Native Cellulose—Formation of Alkali Cellulose. A. Breguet, R. Viatte, and H. Perra. (VI, p. 657.)

Absorption and Fixation of Caustic Soda from Alkaline Solutions by Viscose Rayon. A. Breguet, R. Viatte, and H. Perra. (VI, p. 658.)

Effects of Yarn Irregularity in Dyeing and Finishing. R. G. Fargher, H. M. Taylor, and F. W. Thomas. (VIII, p. 660.)

Pad Dyeing of Fabrics made from Sized Spun Staple Fibres of an Organic Derivative of Cellulose followed by Desizing. W. T. Normand and Celanese Corpn. of America. (VIII, p. 661.)

Printing or Dyeing Superpolyamide Fibres. Ciba Ltd. (IX, p. 661.)

XI-PAPER AND OTHER CELLULOSIC PRODUCTS

Properties of Solutions of Cellulose Acetate. A. B. Pakshyer and R. I. Dolinin. J. Appl. Chem. Pakshyer and R. I. Dolinin. J. (U.S.S.R.), 23, 775-784 (July 1950).

Viscosity and density determinations were made on solutions of cellulose acetate preparations, viz. cellulose triacetate, made by the heterogeneous method, and two varieties of secondary acetate. The solvents used for the triacetate were glacial acetic acid, methylene chloride, 90% phenol, and 85: 15 tetrachloroethane-alcohol. the secondary acetates the solvents used were acetone, aniline, 80% formic acid, 80:20 methyl ethyl ketone-alcohol, and 85:15 tetrachloroethane-alcohol. Tables are given showing the specific contraction in volume accompanying the dissolution of the cellulose acetate, the

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apparent density of the cellulose acetate calculated on the basis of an additive law of mixture, and the specific and intrinsic viscosities of the solutions. A comparison of solutions in different solvents shows that the higher the apparent density and volume contraction, the lower the specific and intrinsic viscosities. Thus, solvents may be placed in a series corresponding to rising apparent density, and hence to falling intrinsic viscosity, viz. for triacetate—chlorinated hydrocarbons, phenols, carboxylic acids; and for secondary acetate- aromatic amines, carboxylic acids, phenols and alcohols, ketones. The apparent density of cellulose acetate falls as the concn. of the soln. is increased, particularly for solutions in the more powerful solvents. These results, together with data on the apparent density when immersed in non-solvents, are interpreted in terms of the degree of solvation of the polar groups of the macro-molecule. A high degree of solvation leads to a greater freedom of movement within the chains, resulting not only in a lower intrinsic viscosity, but also in a more compact disposition of atoms within the soln., i.e. in an increase in the apparent density of the cellulose acetate. A. E. S.

Etherification of Cellulose, especially Carboxymethylation. S. Rydholm. Svensk Papperstidning, 53, 561-567 (30th Sept. 1950). The carboxymethylation of cellulose has been studied

The carboxymethylation of cellulose has been studied with reference to the distribution of the ether groups on primary and secondary hydroxyls, and comparisons are drawn with previous experimental results on other cellulose ethers. It appears that in the etherification of mercerised cellulose an initial reaction occurs up to a 0·15 degree of substitution, during which only primary hydroxyl groups are etherified. All hydroxyls react subsequently at exactly the same rate up to high degrees of substitution. The distribution of the ether groups on the secondary hydroxyls of the cellulose on carboxylation agrees statistically with sulphoethylation but not with methylation and ethylation. Equations for the substitution of the different hydroxyl groups are deduced, and the causes of the initial selective etherification discussed. S. V. S.

PATENTS

Adhesive Crêpe Paper, Minnesota Mining & Manufacturing Co., W. Kellgren, and J. W. Marschall.

B.P. 643,413.

A flat, porous, and stretchable calendered crêped paper having a reversibly compressed fibre structure characterised by a smoothing down of the crêping wrinkles, a substantial decrease of thickness, and a substantial increase in the density of the body structure is made by calendering down to 80% of the original caliper. The calendered paper is thoroughly impregnated with a water-insoluble flexible and stretchable organic polymer or rubber-resin composition in an organic solvent and then has a stretch value of at least 10%. A normally tacky, pressure-sensitive adhesive may be applied to one side of the sheet, the other side being inactive to the adhesive coating, permitting unwinding from rolls without delamination or offsetting of adhesive.

Watermarking Paper. J. D. MacLaurin. B.P. 643,430. A watermarking or printing attachment for Fourdrinier machines comprises a belt, and means for supporting it to travel in a path overlying the wire and in synchronism with it, the belt having openings in it corresponding to the marks to be formed, through which pressure is applied to form a mark in the paper. Colour, e.g. white pigment, may be applied through the belt openings and the pressure applied by a supply of pressure fluid overlying the belt, e.g.. an air blast directed from a nozzle towards the belt openings.

S. V. S.

Glycol Monosulphates—Flameproofing Agents for Paper. W. M. Fuchs and E. Gavatin. U.S.P. 2.511.911.

U.S.P. 2,511,911.

Glycol monosulphates having a C : OH ratio of 1-2 : 1 are inexpensive flameproofing agents for paper. The treated paper remains soft and flexible. C.O.C.

Cellulose Sulphate. J. C. Thomas and Du Pont. (III, p. 650.)

Calculation of the Molecular Weight of Cellulose from the Viscosity of its Cuprammonium Solution. V. I. Ivanov, O. P. Golova, and B. A. Zakharov. (XIV, p. 666.) Relation between the Values of the Molecular Weight found for Cellulosic Products by the Viscosity Method and by the Sedimentation-Diffusion Method. V. I. Ivanov and B. A. Zakharov. (XIV, p. 666.)

XII— LEATHER; FURS; OTHER PROTEIN MATERIALS

Action of Potassium Chloride on Keratin. J. B. Speakman and E. Whewell. J. Textile Inst., 41, T 329-T 330 (Aug.) and T 410 (Oct. 1950).

Load-extension curves of human-hair fibres are determined in water and in various solutions of KCl. Changes in resistance to extension are calculated for each fibre, and the results shown as a function of R.H. The graph is not identical with that showing similar changes in atmospheres rather than in solutions of different R.H. Thus, fibres immersed in a saturated KCl solution are 29-6% less resistant to extension than fibres in equilibrium with its vapour at the same temperature. The effect is considered to be due to the action of KCl in reducing the attraction between oppositely charged ions in the salt links.

J. W. B.

Swelling and Dissolution of Casein. H. Brintzinger and H. Wolff. Kolloid-Z., 118, 26-27 (July 1950).

The swelling of casein in water is a slow process and is necessary before it will dissolve in alkaline soln. Experiments are described on the effects of various salts, acids, and bases on the speed and degree of swelling and also during the preparation of casein soln. Although acids are very effective, they cannot be used in practice, as a correspondingly increased amount of alkali would be required for dissolution.

B. K.

Near Infra-red Spectra of Proteins and Related Substances. S. Mizushima, T. Shimanouchi, and M. Tsuboi. Nature, 166, 406-407 (2nd Sept. 1950).

The near infra-red spectra of certain peptides, e.g. acetylglycine N-methylamide, are studied, and the data used in support of a folded configuration for polypeptide chains. Two characteristic absorption peaks are found in substances where only one type of hydrogen bonding is possible, which is used in argument against the conclusion of Darmond and Sutherland, that the existence of more than one NH-stretching frequency points to the presence of more than one type of bond.

J. W. B.

PATENTS

Liming of Skins and Hides. S. Payno. B.P. 643,452. The skins or hides are dehaired with an aqueous medium containing only CaO and 0·1-0·8% on the weight of the water of a neutral alkali-metal or Mg salt whose solubility at room temperature is less than that of the corresponding Ca salt. This speeds up liming and yields a leather of enhanced absorption properties for chrome and vegetable tanning agents.

C. O. C.

Blown Oils particularly suitable as Substitutes for Chamois Moellon in preparing Fat-liquoring Agents. Nopco Chemical Co. B.P. 643,403. An unsaturated non- or semi-drying oil is blown with air at 30–50°c. in presence of water. The highly hydroxylated

at 30-50°c, in presence of water. The highly hydroxylated products have marked hydrophilic properties and in addition to their use on leather may be used in finishes for textiles and paper.

C. O. C.

XIII—RUBBER; RESINS; PLASTICS

PATENT

Wrinkle-textured Films. H. A. Toulmin and New Wrinkle Inc. U.S.P. 2,511,024.

A layer of a solution of a non-wrinkling thermoplastic resin is spread over a support with a design. Portions of the film are then heated until a skin is formed on them, and then water is applied to the whole film, causing the skinned areas to assume a wrinkled texture.

C. O. C.

Stabilising Thermoplastic Cellulose Ether Compositions. Hercules Powder Co., W. W. Koch, and A. L. Rummelsburg. (III, p. 651.)

Metallic Coatings on Non-metallic Materials. G. J. Kmecik. (X, p. 663.)

XIV—ANALYSIS; TESTING; APPARATUS

Destruction of Organic Matter by Acid Ashing. G. R. Sutcliffe. J. Textile Inst., 41, T 196-T 197 (May 1950).

With reference to the destruction of organic matter by acid ashing (Hamlin, *ibid.*, **40**, T 343 (1949)) it is suggested that the method is dangerous where it is known that the organic material is resistant to the action of hot nitric acid. Three examples are quoted in which organic material was not readily oxidised by nitric acid. H. K.

Improved Method for the Determination of Iodine Numbers. G. H. Benham and L. Klee. J. Amer. Oil Chem. Soc., 27, 127-129 (April 1950).
 The method is a modification of that of Rosenmund and

Kuhnheim (Z. Untersuch. Nahr. Genvss., 46, 154,(1923) and Runnem (Z. Uniersuch. Nahr. Genvss., 46, 154,(1923) and Ber., 56, 1262 (1923)). With one easily prepared and stable reagent, consistent and repeatable iodine values are obtained in 1 min. with all ordinary non-conjugated fats and oils. The oil in CCl₄ is treated with 0·1 x. bromine dissolved in a mixture of acetic acid, sulphuric acid, and pyridine, and mercuric acetate in glacial acetic acid is then added. The solution is titrated with 0·1x acidium. then added. The solution is titrated with 0.1N. sodium thiosulphate in the usual way after addition of KI. Blanks in the absence of oil must be carried out. F. F. E.

Comparison of Two Methods of Testing Detergents.
G. E. Barker and C. R. Kern. J. Amer. Oil Chem. Soc., 27, 113-116 (April 1950).
It is shown that the method involving the measurement

of light reflectance of soiled fabrics before and after washing and the method involving the determination of the light transmission of the wash liquors give results with a typical non-ionic detergent and a typical anionic detergent which lead essentially to the same conclusions. With a tallow soap the two methods do not give comparable results. simple experimental method which indicates the applicability of the latter method has been devised. F. F

Proposed Change in the A.A.T.C.C. Test Method for Rewetting Agents, C. R. Blumenstein. Amer. Dyestuff Rep., 39, 317-320 (15th May 1950).

Experiments have shown that the A.A.T.C.C. test method for rewetting agents gives widely varying results if the test patterns are impregnated at different temperatures. Many rewetting agents which show up poorly at 20°c. are greatly improved if impregnated at 70°c., and it is suggested that this latter temperature be adopted, as this would be more in line with plant practice. The effects of conditioning, ageing, added starch, and test-droplet size on rewetting speed were also studied.

A. S. F.

New Colorimetric Reaction of D.D.T. A. Quintana y Mari and A. M. C. Capella, Bol. Inst. nacl. Invest. agron. (Madrid), No. 15, 229-248 (1946): Chem. Abs., 44, 7477 (25th Aug. 1950).

Determination of D.D.T. in Commercial Preparations and in presence of Pyrethrin and Colouring Matter. A. Davidova. Rend. Ist. super. Sanitá, 13, 167-173 (1950): Chem. Abs., 44, 7479 (25th Aug. 1967).

Mix the product with petroleum ether and talcum to make a dry powder, extract with dil. acetone, dry the solution with Na₂SO₄, distil off the acetone, extract the residue with ether, remove pyrethrin and colouring matter with active charcoal, and evaporate the ether. C.O.C.

Computation Method for Leaching Processes. W. Wiegand. Z. Ver. deut. Ing., Verfahrenstech., No. 4, 117-120 (1950): Chem. Abs., 44, 7095 (25th Aug.

A graphical method based on an experimental leaching curve is described.

Identification of Dyes by X-Ray Powder Diffraction.
G. Susich. Anal. Chem., 22, 425-430 (1950): J.
Textile Inst., 41, A356 (July 1950).
An account is given of the identification of dyes by
X-ray powder diffraction. The difficulties arising from
polymorphism and the sensitivity, limitations, and
applications of the method are discussed. X-ray analysis is
compared with other methods of identification of dyes. compared with other methods of identification of dyes, such as chemical identification, dye tests, and heated specimen microscopy. X-ray patterns of various dyes C. J. W. H. are shown.

Gloss Measurements on Fabrics. R. G. Quynn, E. J. Bernet, and E. K. Fischer. Text. Research J., 20, 492-509 (July 1950).

Using a goniophotometer, the reflectance of a group of fabrics has been measured, and the results are presented names has been measured, and the results are presented as curves relating % reflectance to scanning angle and computed gloss numbers and are compared with visual ratings by different observers. Fabric specimens of the same construction provide curves of similar shape, the colour affecting only the total reflectance. The greatest light scattering of incident light occurs with pile fabrics, which also have a low visual gloss. Compared with other surfaces such as papers, engagelled panels, are fabrica are of low such as papers, enamelled panels, etc., fabrics are of low gloss. The subjective sensation of gloss has been correlated with various physical terms, but the successful expression of gloss in terms of a simple numerical factor derived from physical data appears extremely unlikely. P. C.

New Technique for Cutting Very Thin Sections and its Application to Electron Microscopy. S. B. Newman. ASTM Bulletin, No. 163, 57-60 (Jan. 1950); Text. Manuf., 76, 165-167 (April 1950).

The new technique involves holding the specimen, embedded in polymerised butyl methacrylate, in a brass block. This block, after cooling with carbon dioxide, is allowed to expand, thus advancing the specimen, which is cut by means of a standard laboratory type of microtome. The specimens are flattened by placing in a dioxan-water mixture, and the polymer is dissolved off with toluene. The thickness of such specimens is a few tenths of a micron. The thickness of such specimens is a few tenths of a micron, and may be controlled by the interval between stroking the specimen past the knife edge. A very important factor is proper knife sharpness. The knife was first ground and polished, and then finished, first on a tension strop, and then on a back strop, both strops being charged with fine diamond dust of particle size $0.0-0.5~\mu$. Electron-micrographs of fibres are reproduced. W. J. M.

Quantitative Study of Resilience. L. F. Beste and R. M. Hoffman. Text. Research J., 20, 441-453 (July 1950).

The type of resiliency is defined in terms of stiffness or Young's modulus and diminishing modulus. "Compliance ratio" is proposed as a practical measure of diminishing modulus on the stress-strain curve. The results of measurements of stiffness and compliance ratio are given from the stress and compliance ratio are given. for various fibres and are plotted on a resiliency map. Wool has a relatively low modulus and high compliance ratio, whereas the reverse is true of silk. Nylon has a low modulus coupled with a low compliance ratio. Conditions of preparation of the man-made fibres influence the or preparation of the man-made fibres influence the position they occupy on the resiliency map. The extent of resiliency is governed by the ability of fibres or fabrics to recover from deformation. The correlation of fibre with fabric recovery is discussed, and some results on various fibres are given.

Rôle of the Cationic Ash of Jute Fibre in its Acid Value Determination. H. Chatterjee. J. Textile Inst., 41, T 243-T 248 (July 1950).

Analyses show that about 70% of the ash of jute fibre is cationic. It is necessary to free the fibre from basic ions before estimating acid values by the silver absorption method. The silver absorptions of fibres blocked with various metals show that Na ions have some affinity in presence of Ag ions, whilst Ca. Ba. and Mg ions have presence of Ag ions, whilst Ca, Ba, and Mg ions have higher affinities than Ag ions. F. A.

Determination of the Lignin Content of Jute. H. J. Callow. J. Textile Inst., 41, r 255-r 266 (July 1950). Two reactions take place when lignin is determined by the 72% sulphuric acid method. Carbohydrates are removed by hydrolysis, whilst the furfuraldehyde liberated from hemicelluloses forms acid-insoluble complexes with the lignin. The curve relating yield of residue to time of treatment shows a minimum value when most of the treatment shows a minimum value when most of the carbohydrate is removed and the amount of lignin-furfural complex formed is small. For accurate determinations the acid treatments are made for times greater than that corresponding to the minimum value, and the results extrapolated to zero time. For rapid determinations a treatment is carried out at 25°c, for 1-1½ hr.; this gives a solve does to the obstitute with the product of the obstitute with the second content of the content o value close to that obtained by the extrapolation method.

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Radioactive Technique for Micro-estimation of a-Amino Acids and its Application to Paper Partition Chromatograms. S. Blackburn and A. Robson. Chem. and Ind., 614-615 (12th August

The quantitative reaction between amino acids and a The quantitative reaction between ammo acids and a copper phosphate suspension to give complexes generally of the type (H₄N·CHR·COO)₅Cu (Pope and Stevens, Biochem. J., 42, lix (1948)) has been adapted for a copper phosphate suspension containing ³⁴Cu (half-life 12·8 hr.), the copper in the complex being determined by counting beneath an end-window counter to a statistical error of < 2%. A technique similar to that of Martin and Mittelmann (Biochem. J., 43, 353 (1948)) is described for the determination of micro amounts of amino acids after determination of micro amounts of amino acids after separation on paper chromatograms. Paper cuts from the latter were immersed in 0-18 M-Na₂HPO₄ solution in stoppered test tubes, allowed to stand overnight, and then treated with the copper phosphate suspension above, and the counts given by the copper complexes formed were then determined. A curve (linear) is given for alanine showing counts against amount of amino acid. The accuracy compares favourably with that of other methods. H. H. H.

Amino-acid Separations by Use of a Strong-base Resin. C. W. Davies, R. B. Hughes, and S. M. Partridge. J.C.S., 2285-2287 (Sept. 1950). The possible value of an ion-exchange resin of strong

base (quaternary ammonium) type for the separation of base (quaternary ammonium) type for the separation of amino acid mixtures has been examined for Dowex 2. This resin was characterised by the method of Partridge and Westall (*Biochem. J.*, 1949, 44, 418 (1949)), and by means of it good separations of leucine—glutamic acid and leucine—methionine mixtures were effected. H. H. H.

Determination of Degree of Polymerisation of Regenerated Cellulose, and Quantitative Separa-tion of Cotton from Rayon. E. Cerbaro. Boll. cotoniera, 37, 56-57 (1942): Chem. Abs., 44, 7534 (25th Aug. 1950).

Disintegrated fibre (50–100 mg.) is agitated with 100 c.c. of 10% aq. NaOH at -5° c. for 30 min. and filtered on an 11 G3 sintered glass filter. The dissolved cellulose is determined by oxidation with $K_{..}Cr_{2}O_{7}$ (Schwalbe and Seiber method) and the η of the solution in a Schott and Gen capillary viscometer. The degree of polymerisation (D.P.) is then calculated from Staudinger's equation, taking the value 7×10^{-4} for the constant K_m , when D.P. = 150-600. The method is also used to separate cotton from rayon by selective dissolution of the latter in aq. NaOH. The residue is washed with water and dil. acetic acid and dissolved in aq. cuprammonium soln., and the cotton determined by the viscosity method. C. O. C.

Differentiation of Cellulose Ethers and Cellulose Ether Glycollic Acids. R. Neu. Fette u. Seifen, 52, 23 (1950): Chem. Abs., 44, 7531 (25th Aug. 1950). Zephirol (dimethylalkylbenzylammonium chloride) solution yields a white precipitate with cellulose ether glycollic acids. Cellulose ethers do not react. The reaction is very

Tables for Use in computing Small Colour Differences. D. Nickerson. Amer. Dyestuff Rep., 39, 541-546 (21st Aug. 1950).

sensitive.

Alkali-metal salts do not interfere. C. O. C.

Tables have been computed to convert the C.I.E. tristimulus values (X, Y, Z) into rectangular co-ordinates based on the Munsell colour system. By inserting these latter values in the Adams formula a figure for the colour difference is obtained. In this way it is possible to refer to colour differences in numerical terms. The numerical transformation from the tristimulus values to the colour difference between two patterns takes about 90 sec. The tristimulus values may, in turn, be obtained from the spectral reflection curve of the pattern. W. J. M.

Rapid Method for Determining Mildew Susceptibility of Materials and Disinfecting Activity of Compounds. R. G. H. Siu and G. R. Mandels. Text. Research J., 20, 516–518 (July 1950). The method is based on a measurement of growth of the

micro-organism by manometric determination of total oxygen absorbed during growth. The apparatus consists of a differential manometer coupled to a control and an experimental flask. The culture flasks contain 50 ml. mineral-salts agar and have suspended in them a cup containing 1.5 ml. of 10% potassium hydroxide and a filter-paper wick. The apparatus is placed in an incubator at 30°c. A fabric disc 7 cm. in diameter is placed on the agar surface in the experimental flask and inoculated with 1 ml. of a spore suspension of *Myrothecium verrucaria* U.S.D.A. 1334·2. Both experimental and control flasks are then attached to the manometer by the connectors, and after an equilibration period of 3 hr. the stopcocks are closed. During growth the organism absorbs oxygen from the gas space in the flask, which causes a decrease in The potassium hydroxide absorbs any carbon pressure. dioxide produced. Changes in the pressure are used as the criterion of susceptibility to mildew.

Calculation of the Molecular Weight of Cellulose from the Viscosity of its Cuprammonium Solution. V. I. Ivanov, O. P. Golova, and B. A. Zakharov. Izvestiya Akad. Nauk S.S.S.R., Otdel. Khim. Nauk, 408-411 (July-Aug. 1950).

In the determination of the mol. wt. of a cellulose preparation from viscosity measurements in cuprammonium soln. the experimental conditions are of prime importance. By employing still more rigorous methods of oxygen exclusion during the preparation of the cuprammonium soln. than those employed by Schulz et al. (Z. phys. Chem., 52, 23 (1942)), the authors have obtained a threefold increase in the value of the mol. wt. of cotton They now consider the effect of uncertainties cellulose. regarding the value of the Staudinger constant on the value obtained for the mol. wt., and show it to be of relatively minor importance when the variations arising from experimental conditions are taken into account.

Relation between the Values of the Molecular Weight found for Cellulosic Products by the Viscosity Method and by the Sedimentation-Diffusion Method. V. I. Ivanov and B. A. Zakharov. Doklady Akad. Nauk S.S.S.R., 72, 1063-1065 (21st June 1950).

If M_8 is the mol. wt. of a cellulose preparation, determined in cuprammonium soln. from measurements of sedimentation and diffusion, and M_Y is the value obtained from viscosity measurements on the same soln., then the ratio $M_s/M_{_{\overline{V}}}$ is known to be > 1 and to vary with the degree of polymerisation of the preparation from 4–6 for unmodified natural fibres down to 2 or less for commercial rayons. It is now shown, by an examination of the available data for a considerable range of cellulose preparations, that the relationship— $M_8=1.97\,[\eta]^{0.333}\mathrm{M}_{\Psi}$ is very closely obeyed, $[\eta]$ being the intrinsic viscosity based on concentrations in g./100 c.c. In the calculation of $M_{\rm v}$ the Staudinger const. is taken as 5.0×10^{-4} . A. E. S.

Electrographic Printing for Coating Control. M. Kronstein. Chim. Peintures, 13, 151, 152 (1950): Chem. Abs., 44, 6655 (25th July 1950).

Water permeability and other properties of an organic coating are evaluated by soaking paper in an aq. soln. of an electrolyte, pressing it on the sample, applying 4–6 v. D.C. through the assembly, and developing the resulting print.

Detergency Comparator. C. L. Nutting. Amer. Dye-stuff Rep., 39, P 260-P 261 (17th April 1950). The comparator has been designed to give high con-

centrations and low bath ratio with the object of simulating good plant practice in order to assess the effectiveness of detergents in wool finishing and manufacture. essentially a pair of dolly washers reduced to laboratory size, with provision for accurate control of temperature and other process variables designed to give a considerable flexibility of use.

Standard Scouring Process for Loose Wool.

Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25. Richtlinienblatt A 2102. Textil-Rund., 5, 281 (July 1950).

Details are given of a standard scouring process for loose wool to remove perspiration and dirt before estimating the commercial wt. of the wool or assessing its physical properties. B. K.

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Standard Scouring Process for Wool containing Carding and Spinning Oils. Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25. Richtlinienblatt A 2103. Textil-

Rund., 5, 282 (July 1950).

Wool is oiled after scouring to facilitate further processing, and the oils used have to be removed before estimating the commercial wt. or assessing its physical properties. Standard scouring processes are detailed for removing the oil from slubbing and yarns.

B. K.

Rapid Method for Control of Wool Scouring. Robinet. Teintex, 15, 326-329 (July 1950).

Residual grease in wool is estimated by running 100 ml. of ether slowly through a tube containing a 1-g. sample of material. The ether emerges dropwise from a capillary and falls on to a heated watch glass, where it is immediately evaporated. The extraction requires only 25 min. The new method usually gives slightly lower results than the longer standard method, but it is sufficiently accurate for works control purposes. The technique of sampling the material before testing is described.

Fastness to Dry Cleaning of Dyeings and Prints. Schweizerischer Verband für die Materialprüfungen der Technik, Kommission 25. Richtlinienblatt A 2525.

Textil-Rund., 5, 319 (Aug. 1950). The test pieces are treated for 30 min. at $20\pm2^{\circ}\mathrm{c}$. in trichloroethylene. A liquor ratio of 40 : 1 is used, and the material is kept moving during the period of test. The test pieces are squeezed out and air-dried at 100°c. Trichloroethylene can be replaced by other solvents, such as perchloroethylene, but the product used must be specified and the drying temp. altered accordingly.

B. K. and the drying temp, altered accordingly.

Fastness to Potting of Dyeings and Prints.
Schweizerischer Verband für die Materialprüfungen
der Technik, Kommission 25. Richtlinienblatt A 2575.
Textil-Rund., 5, 320 (Aug. 1950).
The test material is wound round a glass rod, boiled

for 1 hr. in distilled water using a liquor ratio of 100:1, and removed from the rod; the dyed and undyed materials are separated and air-dried at a max. of 60° c. B. K.

Methods of Determining the Water Vapour Permeability of Laminæ. A. C. Newns. J. Textile Inst., 41, T 269-T 308 (Aug. 1950).

A literature survey is made of the experimental methods that have been used for investigating the diffusion of water vapour through laminar materials. Apparatus is briefly described, together with analytical methods, calculation of results, and sources of error, and it is considered that for general purposes the weighed cell methods are most suit-There are 164 references.

New Microscopic Tests for the Identification of Damage to Wool and Silk. E. Kornreich. J. Textile Inst., 41, T 321-T 328 (Aug. 1950).

A scheme of analysis based on staining and microscopic examination enables distinction to be made between acid, alkali, peroxide, alkaline hypochlorite, mechanical, and scorch damage of wool, and between hypochlorite, scorch, and alkali damage of silk. Wool is first submitted to a modified Krais test, which permits a preliminary division to be made; subdivision is completed by applications of Methylene Blue and Indigo Carmine staining tests. Silk is treated with cupriethylenediamine, the swelling being studied, and then stained with Methylene Blue. J. W. B.

PATENTS

Electrolytic Investigation of Solutions. Brno N. P. B.P. 643,336.

Apparatus is described for the determination of the first differential derivative of a current-voltage curve instead of the curve itself, such an analysis being in consequence not limited by the width of the recording paper, and also being capable of determining small amounts of metals, e.g. Ni, in presence of a great excess of others, e.g. Cu. J. W. B.

Rotational Viscometers. Dobbie McInnes Ltd. and A. R. Boyle. B.P. 643,552.

A pipette is formed from a capillary tube (of internal diameter 0.2-1.0 mm.) and marked with a scale, each division of which corresponds to a surface tension of 1 dyne/cm. at a determined temperature and pressure. The surface tension is indicated by the level to which the The surface tension is indicated by the vertically into it. C. O. C.

Identifying Colour. D. W. Thomasson. B.P. 643,396. Apparatus which measures colour to a high degree of accuracy comprises a source of light, means for deriving a colour spectrum from that source, means for illuminating the sample under test with different successive parts of that spectrum, and means for collecting light reflected from or transmitted by the sample. An indicator is deflected in one of two co-ordinate directions in dependence upon the reflected or transmitted light from the sample and in the other co-ordinate direction in synchronism with the successive illuminations of the sample by the spectrum.
C. O. C.

Analysing the Light-reflecting and Light-scattering
Properties of a Surface, C. A. Chester and Wiggins
Teape & Co. (1919) Ltd.

A light-sensitive cell receives the light reflected or
scattered from the surface being examined while the latter
is rotated on an axis, within or closely parallel to itself, at
a high speed related to the frequency governing the
operation of an electronic oscilloscope. The oscilloscope is
associated with the light cell so that the intensity of the
light coming from the surface throughout its rotation may light coming from the surface throughout its rotation may be indicated on the oscilloscope screen directly as a C. O. C. graphic curve.

Drying and Conditioning of Dyers' Bits. B.P. 642,132. Hunt Machine Co.

A heated housing in which there is an opening contains a rotor mounted on a movable support so that it can be pulled outside the housing. The rotor has means to support the material to be dried and is driven so as to whirl it. There are two doors movable with the rotor, one to close the opening into the housing when the rotor is outside the housing and the other to close it when the rotor is inside the housing. The rotor may be driven both when it is inside and outside the housing. C. O. C.

Humidity or Dew Point Measuring Apparatus. Illinois Testing Laboratories Inc. B.P. 641,555.

Manufacture and Testing of Absorbent Cotton [and Other Fibres]. E. Cerbaro. (X, p. 662.)

Mercerisation of Textiles containing Spun Viscose Rayon—Identification of Mercerised Viscose Rayon. E. Cerbaro. (X, p. 662).

XV- MISCELLANEOUS

Photocopying Processes for the Research Worker. B. de Gorter. Research, 3, 417-420 (Sept. 1950). A review of the methods now available for the copying of books and documents.

PATENTS Oxide Coatings on Aluminium.

Aluminum Co. of America.

U.S.P. 2,504,434
Uniform and dyeable coatings are obtained by treat R. B. Mason and U.S.P. 2,504,434. ment in an aqueous bath containing 0.5-6.0% by weight of an alkali-metal carbonate, enough of a water-soluble aluminium salt to give the bath an aluminium content of not < 0.05%, and a compound which reacts with the aluminium salt to make the bath alkaline and to yield an aluminium complex of low solubility readily precipitated as hydrated alumina. C. O. C.

Wood Stains. Chadeloid Corpn.

B.P. 641,598.

The stains obtained by dissolving a dye in 2-amino-2-methyl-1-propanol, furfuryl alcohol, or tetrahydrofurfuryl alcohol and a thinner, e.g. an alcohol and an aromatic hydrocarbon, give uniform staining of wood, dry rapidly, and do not raise the grain.

C. O. C.



